Technical University of Liberec

Faculty of Textile Engineering

DIPLOMA THESIS

2010 **Mavela Luthuli**

Technical University of Liberec

Faculty of Textile Engineering

Department of Textile Chemistry

Dyeing of Special fibers by the Sol Gel Method

Mavela Luthuli

Supervisor: doc. Ing. Jakub Wiener, Ph.D.

Consultant: Ing. Marie Štěpánková

Number of pages: 82

Number of figures: 34

Number of tables: 13

Number of appendices: 1

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Acknowledgements

I would first like to thank Assoc.Prof. Jakub Wiener Msc.PhD for his invaluable inspiration, perseverance and guidance throughout the course of this research. Many thanks to the laboratory staff, thanks for assisting with tests and operations of equipments.

I am deeply grateful to Department of Economic Development of the South African Government for providing funding for my graduate studies. Many thanks to my friends and family who have inspired me all the way through my diploma work, especial thanks to my father who has guided and supported me with knowledge of how to tackle and solve problems which relate to post-graduate studies.

Abstract

This is a study of dyeing of special fibers using a special solvent which is believed to form a film by bonding with the surface of the glass fibers. The film formed enables the selected dyes such as the acids, disperse and cationic to adhere to the fiber surface by forming dye-film bonds on the coated fibers. The process of dyeing and coating of fiber with this solvent occurs simultaneously resulting to reasonable dye fastnesses to the fibers at the same time bright and dark shades can be obtained. The solvent used is based on the blending of 3-trimethoxysily and propylmethacrylate in combination with isopropylnol and complementary solvents (water, HCl, BPO). Positive results have been obtained in this brief study although further data may be c collected by conducting more laboratory experiments using different substrates and the TMSPM (SOL GEL) solvent.

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Introduction

Special fibers are widely used in the field of technical fabrics where fiber properties such as mechanical, tensile, thermal etc. are of great importance. The method of dyeing must be such that, there is no negative influence on the fiber properties. Things like the handle and stiffness are of minor importance especially when it comes to technical applications of fibers; it's another matter regarding apparel and home textiles. This study is concerned with coloration of special fibers in general; laboratory work will be conducted only for glass fibers.

In modern world glass fibers can be used for many applications because of their strength and high thermal resistance as well as resistance to corrosive solvents. The glass fiber strands can be compiled at the bushing to make direct rovings that, when unreeled do not have a twist and are ideal for advanced composites made from prepregs, or by filament winding and pultrusion. In general many forms of glass fiber products maybe are produced by different assemblies or technologies. The main problems associated with the glass fiber textile production are to obtain variety of colours with suitable application fastnesses.

Aim of this study

There are many problems associated with coloration of special fibers because of their fiber chemical contents. Special fibres normally have a glassy-like surface and high Tg temperatures which makes it impossible for the dye molecule to penetrate the surface of the fibers especially when using water (H_2O) as a solvent. Due to these problems, the dyeings of these fibers has added to production costs because special solvents and techniques are used to obtain reasonable fastness properties with limited color shades. There are many possible reasons why special fibers are difficult to dye, these will be discussed in details as the study continues and laboratory experiments will be conducted to provide this study with concrete evidence.

The main aim of this study is to discuss existing literature about dyeing of special fibers using special solvents, whilst at the same time comparing and viewing the dyeing processes and techniques for selected other high performance fibers such as glass, aramides and polypropylene fibers, these are selected because there is a great deal of difficulty experienced by the Dyers during the colorations of these fibers. These difficulties may be due to these fibers having a high Tg temperatures or they may be due to the polymer bonds within the fiber structures or both cases may be applicable. In this study another method of dyeing glass fibers will be evaluated, hopefully with success its can be also be applied to other fibers mentioned above.

LITERATURE REVIEW

1.1 THE OBJECTIVES OF COLOURATION OF TEXTILES

The objectives of coloration treatments are first to produce the desired colour in dyeing and colours in the coloured design image in printing on the textile. Second, coloration treatments are to ensure that the necessary colour fastness requirements for the end-use are achieved. Third, the whole operation should be carried out at the lowest cost commensurate with obtaining the desired technical performance. After dyeing, the levelness and uniformity of colour across the width and along the length of a technical textile fabric must be within the defined colour tolerances agreed between the dyer and the customer prior to coloration. Preservation of the original appearance and quality of the technical textile prior to coloration is also essential in order to ensure that the technical textile is of marketable quality.

The following selected fibres will be discussed in details because these represent a group of technical textile fibres which have been used for years in for various high performance requirements, included in these are some of the conventional high performance fibres. The aim of this study is to understand and find possible ways of improving of dyeing high performance fibres such as glass and aramides, the following literature is to provide the background of how textile fibre materials and how does the coloration process takes place amongst different fibre of different/same polymer composition.

1.2 GENERAL PRINCIPLES OF DYENG

Long ago dyeing was considered as an artist process in which a dyer was like a painter, he was only able to use the dyes offered to him by nature to obtain limited shades and hues. It was in the turn of the 19 century that a vast variety of dyes were developed for natural fibres, soon after that the synthetic fibres were developed so as the dyes suitable for the coloration of the synthetics. With this knowledge dyeing was transformed from being an artist job to a technological aspect. Over the following years studies and experiments have been conducted to explain the exact phenomena of dyeing.

What has been observed by many scholars of this field is that during dyeing the dye molecule passes through the following phases ***See figure1***: movement from the liquid towards the fibre (diffusion of dye in the dyebath stage), and than it passes from the liquid to a solid stage (absorption), followed by the dye penetrating the surface of the fibre (diffusion to the fibre stage), followed by the formation of bonds between the dye molecule and the fibre molecules (fixation stage), this is considered as the general fundamentals of dyeing. It is at this point that once the dye molecules have been bonded to the fibre that, the dyeing process is considered to be completed.

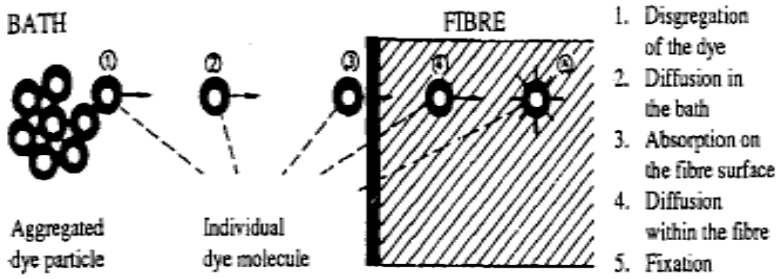

Figure 1.1: *diagram of the phases of dyeing*

The above mentioned phases are only the highlights of what happens in the process of dyeing, in actual fact there are many stages and exfactors which affect reproducibility of colour on the textile substrate with suitable depth and appropriate fastness properties. Some of the factors in involved in the dyeing phenomena are: rate of dyeing and equilibrium, dye migration and dyeing sorption isotherms.[1] More detailed notes about the dyeing phenomena, between the dye molecule and the fibre chemical composition will be discussed further especially for synthetic fibres such as the glass and other high performance textile fibres.

1.2.1 Rate of dyeing

In most practical dyeing processes the temperature increases during dyeing. The exhaustion-time curves have a complex shape which depends on the specific temperature-time sequence adopted, as for example in **Figure 1.2**. The rate of dyeing often accelerates at first, and then gradually decreases to zero if the final temperature is held constant. If the final temperature is held constant for a sufficient time, and there are no serious structural changes in the fibre, and there is no significant decomposition of dyebath chemicals or of the fibre, then a time-independent equilibrium state will be reached (t→∞).[2]

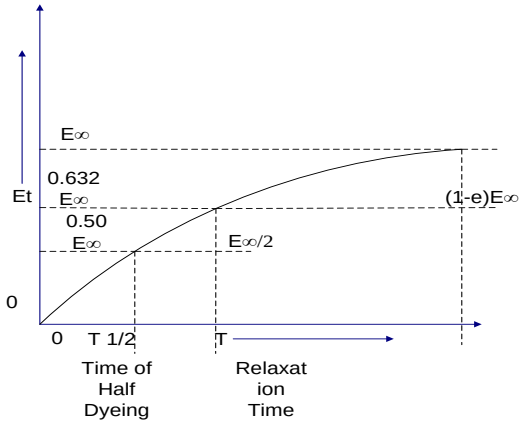

Figure 1. 2*: Rate of dyeing to reach equilibrium exhaust state*

1.2.2 Dyeing equilibrium

At the end of the dyeing process, a thermodynamic equilibrium is established between the dye dissolved in the liquor and the dye that has diffused into the fibre. The relationship between the dye concentration in the liquor and on the fibre is roughly described by the well-known Langmuir and Nernst isotherms. A finite time is required to achieve this state of equilibrium. The time required depends on the substrate, the dyes and the process parameters. This process can be described by the laws of dyestuff diffusion.

The purpose of the following isotherms is to study the variations in the concentrations of the dye in the fibre and their relations in the concentration of the dye in the dyebath.

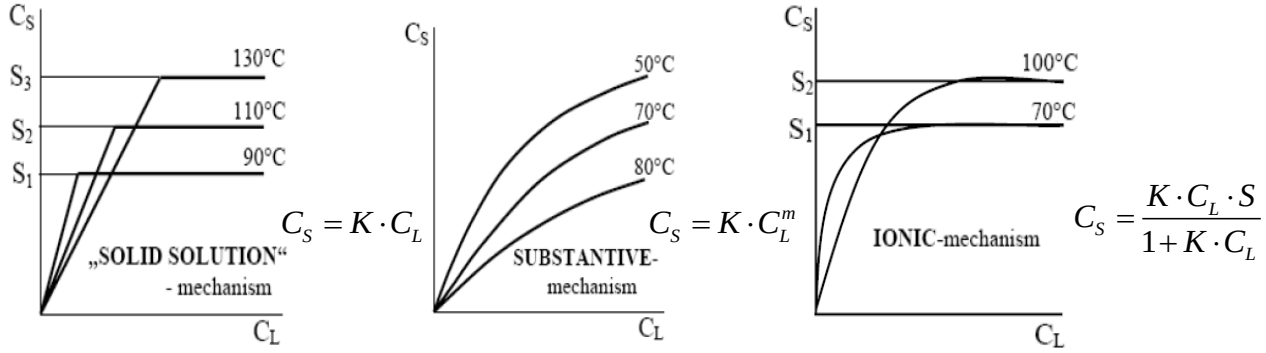

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Figure 1.3: *Sorption Isotherms used for understanding how different dyes are controlled by what mechanism during the process of dyeing it's also related to dye affinity for the fibre*.

Table 1:1: for explaining the above absorption Isotherms

Mechanism of sorption	Solid Solution	Substantive	Ionic
Dye/fiber system (only the main case)	Disperse dyes on hydrophobic fibers	Substantive dyes on cellulose	Acid dyes on wool and PA Or cationic dyes on acrylics
Sorption influenced by: pH neutral electrolyte	minimal minimal	low high	high low
Typical marks	Dispersing agents complicate the linear course of isotherm	Without "salt" only low sorption. S-value unavailable	In low concentration: high %Exhaustions linear relation

1.2.2.1 Temperature influence on equilibrium dyeing

Rate of dyeing accelerates and increases visibly exponentially with an increase in temperature. As a result the dye sorption on fibers in equilibrium or near the equilibrium state undergoes a slight decrease in rate of dye adsorption to the fiber. The dye affinity of the dyes in most cases sinks as the dyeing temperature increases. This can be illustrated by the crossing of curves in the graph below.

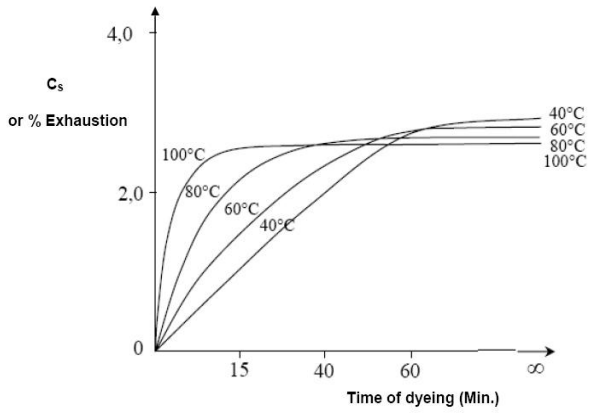


Figure 1.4: *Crossing of kinetic curves for the dyeing using different temperatures to obtain exhaustion*

This phenomenon is common to the old dyeing technologies where the dyeing process used to be done for long time, as a result the bath gets cold and the exhaustion increases due to the increase in the affinity of dyes for the fiber. It is difficult to reach this stage with the modern dyeing technologies.

1.2.3 Thermodynamics of dyeing

Dye is an exothermic process, where energy is given off during the dyeing process and rate of diffusion of the dye is higher at elevated temperatures. The state of dyeing equilibrium is defined by assemble of microscopic properties which do not vary with the passage of time. These properties might be temperature, pressure and the composition of the dyeing ingredients or else other invariable properties which characterize certain aspects of equilibrium, such as free energy, enthalpy or entropy. Dyeing can thus be described by theories and equations of thermodynamics. Gibbs equations for determine the spontaneity of the reaction processes. [3]

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

ΔG= Gibbs free energy [J.mol-1]

ΔH= Enthalpy [J.mol-1]

T= Temperature [K]

ΔS= Entropy [J.mol-1]

- If ΔG<0 The process is spontaneous
- If ΔG>0 Its a non-spontaneous process but the reverse process would be spontaneous
- If ΔG=0 The system is at equilibrium

1.2.3.1 Chemical potential of dyes in the solution

$$-\Delta\mu^{\circ} = RT \ln \frac{[C]_f}{[C]_s} \qquad (2)$$

$\Delta\mu^{o}$..... is the measure of the driving force of the reaction

R..... is the gas constant (8.314 J/mol.K)

T…… is the temperature (K)

$[C]_f$…….. is the dye concentration in the fiber

$[C]_s$…….. is the dye concentration in the solution

The above equation can be used for highly diluted solutions, in which case it's relevantly easy to obtain the quantitatively differences between the standard chemical potentials. In the majority of dyeing operations it is not possible to substitute activity with concentration; therefore it is necessary to study both dyes in the solution and in the fibre. Dyes in the solution can either be:

(a) not dissociated, in that case the following equation can be used

$$\mu_s = \mu_s{}^{\circ} + RT \ln a_s \qquad (3)$$

(b) Dissociated or ionized, lets assume the dye dissociated according to the following formula:

$$CNa_z \leftrightarrow C^{z+} + zNa^{-} \qquad (4)$$

If the nature of dyes was such that their supplied ions by their dissociation, like H^+, NH_4^+,Ca^+, Cl^- it is evident that the equation would be applied on the bases of the dissociation of these, the formula would be like this[3]:

$$\mu_S = \mu_S{}^\circ + RT \ln [C^{z+}][Na^-] \qquad (5)$$

1.2.3.2 Chemical potential of dyes in the fibre

To analyze the activity of dye in the fibre it is necessary to examine three cases, and these are:

(a) Solid solution: in this case there is the assumption that when the dye dissolves in the fibre there is no dissociation of dye molecules, than the values of the activity can be found by substitution of these concentrations as follow:

$$\mu_f = \mu^\circ_f + RT \ln a_f = u^o_f + RT \ln[C]_f \qquad (6)$$

Where $[C]_f$ is the measurable concentration of dyes expressed in moles/kg of the dry mass of the fibre.

(b) Diffused adsorption: this occurs when the surface of the fibre attracts the dye molecule, this is an inverse function of the distance. If the dye dissociates in the interface, according to the equilibrium its, activity is expressed as the product of the concentrations of its ions:

$$\mu_f = \mu^\circ_f + RT \ln(\frac{[Na^+]_f}{V})^z.(\frac{[C]_f}{V}) \qquad (7)$$

(c) Monomolecular adsorption: for this case, specific sites in the fibre have to be determined which attracts the dye molecules and also retain the dye molecule in such a way that, an already occupied site is not able to attract other moles and be occupied by them.[3]

1.2.3.3 The affinity of dyes

Affinity is the intrinsic property of matter in which a body tends to attract and react with another. Affinity can be expressed by the following equation:

$$-(\mu_s{}^o - \mu^o) = -\Delta\mu^o = RT \ln \frac{C_S}{C_L} \qquad (8)$$

1. $-(\mu_s^o - \mu^o)$ The differences of standard potentials between (fib – bath)

2. $-\Delta\mu^o$ Affinity, the greater is the affinity value (>O) the higher and the faster is the dye exhaustion into the fibre.

3. $\mathrm{RT}\ \ln \frac{C_S}{C_L}$ Concentration of dye in the fibre/concentration of dye in the bath

1.2.4 Kinetics of dyeing

This is a study of how the dyestuff is transported and able to diffuse inside the fibre. In the state of dyeing equilibrium, the dye concentration is always higher in the fibre compared with the dye bath. This could mean in any dyeing system there is a difference in instantaneous chemical potential, a movement of material will take place from the higher toward the lower potential until these become level. Provided the system is homogeneous the difference in concentrations will be sufficient to cause the transportation of matter.

1.2.4.1 Partial processes in bath-dyeing

Particles of dyes (molecules, ions and their aggregates) pass in process of dyeing in successive steps through 4 principal movements:

a) Motion in bath to the fiber surface (diffusion in bath, transport in bath)

b) Diffusion through the boundary layers to the fiber surface,

c) Adsorption on fiber surface,

d) Diffusion into the fiber-interior

a) diffusion in bath, transport in bath

This stage depends on hydrodynamics, how much bath agitation by means of cerculation is being exected on the dyebath.

b) Diffusion through the boundary layers

The boundary layer consists of two thin layers, the hydrodynamic layer on the outer space of the fiber surface and the diffusion layer on top of the fiber surface. The diffusion layer is directly proportionally to the hydrodynamic layer and indirectly proportional to the rate of stream (flow). The boundary layer can be reduced by streaming of fibers streaming mechanism is not constant, if there are some differences in streaming, this can result to unlevel dyeing.

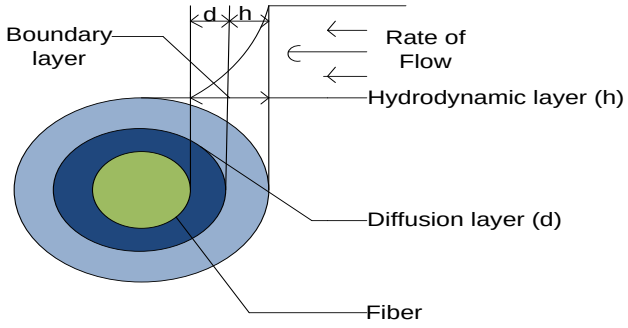


Figure 1.5: *Illustration of the 2 thin layers making the boundary layer.*

c) Adsorption on fiber surface

The dye surface can be saturated by the dye particles in seconds provided the streaming and the dyeing conditions are suitable, the dye penetration and for inside the fiber saturation can take hours. The dye particles diffuse from the adsorbed layer and penetrates the inside of the surface, the rate of penetration depends on the dye concentration on the adsorbed layer on the surface of the fiber. The dye molecule must not be over saturated on the fiber surface that will cause difficulties for the dye particles to penetrate the fiber surface. (Bronze effect= complicated aggregates)

d) Diffusion into the fiber-interior

The dye particle, after penetration they have to diffuse through out the fiber interior resulting to even concentration through the whole fiber. This process takes longer than adsorption of dye molecules on the fiber surface and also if the process is not taken care by correct dyeing parameters unlevellness of dyes may occur. Unlevellness is when the concentrations of dyes through the fiber are not equal; you have dark and light places.

Diffusion inside the fiber is influenced by the following factors:

a) Heat motion of the molecules, with the increase in temperature the diffusion increases dramatically. (Brown motion)

b) Concentration gradient, with the dyebath concentrations at high, dyeing is accelerated to the saturation of the fiber surface layer.

c) Size of dye molecule, the smaller the size of the dye molecule the easier and quicker it is for the dye to penetrate the fiber surface and move around the fiber for bonding.

d) Size and shape of the pores and intermolecular structure of the fiber, diffusion of dye can occur in the amorphous region of the fiber; if the mass of crystalline is increases then the dye molecule will have difficulties to diffuse in the fiber.

e) Orientation of polymer chains reduces the intermolecular distances and so decreases the rate of dye diffusion.

Ficks law of diffusion: In the phase of dyeing the dye distributes concentrically in the fiber in such away that, there is a high concentration of dye paticles on the fiber surface compared with the low or no fiber interior. The existence of a gradient of concentration is the reason why the dyeing migrates towards the centre of the substrate. Ficks law states the flow of the molecule of the dye is directly proportional to the gradient concentration:

$$v = \frac{ds}{dt} = -D.\frac{dc}{dx}.S \qquad (9)$$

ds..... quantity of the substrate

S..... unit area

dt..... time

v..... rate of dyeing

dx..... diffusion distance

Ficks second law: describes changes of concentration penetrating substance C in dependence on time t and place x. For diffusion in direction x Fick deduced:

$$\frac{dc}{dt} = D.\frac{d^2c}{dx^2} \qquad (10)$$

D is a constant of diffusion coefficient ($cm^2.s^{-1}$) in real textile conditions. It's a non ideal characteristic of a substrate, morphology, crystalline, and non Ideal dye solution. Theoretically D-coefficient should not be dependent on concentration.

Ficks laws are not exactly suitable for dyeing because of the increase in approximation for infinity cylinder and radius (r). The following equation is used for the calculating the diffusion coefficient in normal dyeing systems.

$$\frac{C_t}{C_\infty} = 1 - A\exp(-B.F_0) - C\exp(-E.F_0) \qquad (11)$$

$$F_0 = \frac{D.t}{r^2} \quad \textbf{Fourier number} \qquad (12)$$

A, B, C, E constants

D diffusion coefficient [$cm^{2}.s^{-1}$]

C_t, C_∞ dye-concentration on fiber in time (t) and in ∞

t time of dyeing (s)

C_{rt} relative concentration in fiber C_t/C_∞

Fourier values are for the equilibrium exhaustion, and the relative concentration C_{rt} in the fiber is calculated.

The radius (r) or the diameter (d) of the fibre can be determined either directly microscopically, or by calculating using Tex of the fibre. This is done by assuming that the cross section of the fibre is circular, than it is possible to used the following formulary:

$$d = \sqrt{\frac{4 \times tex}{\pi \times \rho}} \quad \textbf{mm}$$

Example of calculation:?? D for the case: 3.5 % dyeing (by 130°C) of PES fibers 0.3 Tex, density (ρ) = 1380 $kg.m^{-3}$. In equilibrium was determining: C_∞ = 31, 5 $mg.g^{-1}$ ~ exhaustion E_∞ = 90 %. After 10 minutes of dyeing found 10.1 $mg.g^{-1}$

Results of the above example:

Time (t: sec)	**Sorption (C_t:$mg.g^{-1}$)**	**C_{rt}**	**F_0**	**D:$cm^2.sec^{-1}$**
600	**10.1**	**0.321**	**0.00032**	**$4{,}4x10^{-13}$**

Square root law: state that the dye concentration in the fiber (exhausted) is proportional to the square root of dyeing time (t). This theory was derived for isothermal dyeing experiment.

$$\frac{C_t}{C_\infty} = 4\sqrt{\frac{D.t}{\pi.r^2}} = tg_\alpha.\sqrt{t} \qquad (14)$$

1.2.5 Dye diffusion into pores of the fibre

Coloration of textiles does not depend only on the dye molecules being attracted to the fibre surface. In natural fibres there are pores on the surface of the fibre and the fibre itself has to types of polymer arrangements crystalline region and amorphous regions, dye molecules pass through the amorphous regions to be bonded inside the fibre. Diffusion into fibers is accelerated by temperature which can also activate the dye molecule to penetrate the fiber , these can be calculated or expresses using the Arrhenius equation below:

Arrhenius equation $$D = D_o \times e^{\left(-\frac{E_a}{R \times T}\right)} \qquad (15)$$

E_a..... activativation energy of diffusion

R..... gas constant

T..... absolute temperature

D_o..... Constant frequency factor values reach $10^{10\text{-}12}$

1.2.6 Dye diffusion into Free-volumes

It is another case all together for the dyeing of synthetic fibres, most synthetic fibres do not have pore like natural fibres for the dye to penetrate easily and the fibres are more crystalline then amorphous, diffusion of dye is due to high temperatures above the Tg of fibres to create free-volumes in order for the dye to penetrate the fibre. The Williams-Landel-Ferry equation (WLF) dependence is used to describe the diffusion mechanism in free-volumes of the polymer formed and destroyed by the temperature fluctuations.

Williams-Landel-Ferry equation (WLF)

$$D_T = D_{Td} \times e\left[\frac{-A \times (T - T_d)}{B + (T - T_d)}\right] \qquad (16)$$

Where D_T and D_{Td} are diffusion coefficient by temperature (T) and transition temperature T_d. The constants were determined for amorphous polymer: A=17.44 and B=51.6.

1.3 DYE FIBER BONDS

Textile fibers come 3 categories:

- Cellulosic, natural and regenerated fibers
- Protein, natural and regenerated fibers
- Synthetic fibers, which are man-made by combination of monomers

Dyes molecules are complex aromatic structures with extended π-electron system, polar constituents, and water solubilising groups as show in the table bellow: [4]

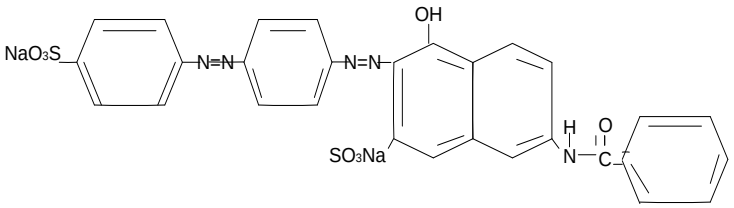
Table 1.2: Dyestuffs solubilising groups and types of dyes

Solubilising groups	**Types of dye**
Permanent	
SO_3 Na (or −COONa)	Direct; acid; chrome mordant; reactive; 1:1metal-complex
$-^{+}NH_2HCL^{-}$, $-^{+}NR_3\ Cl^{-}$	Basic dyes for cellulose; wool; silk; and acrylics
−OH, $-NH_2$, $-SO_2NH_2$	Disperse dyes for cellulose acetate; nylon and polyester fibres; 1:2 metal-complex dyes for wool and nylon
Temporary	
$-O^{-}Na^{+}$	Dyes for cellulose, i.e. naphthols for subsequent Azo coupling on the fibre; vat dyes
Onium groups, e.g.	Phthalocyanine dyes for cellulose
(R=Alk or Ar)	
$-OSO_3\ ^{-}Na^{+}$	Solubilised vat dyes

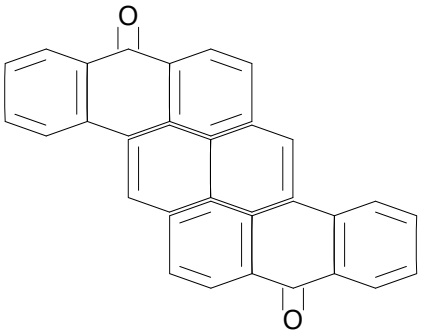
Solubility is essential to enable the dye to penetrate the intermolecular micro-pores of the fibre. In fact dyes should have both big and small molecules in the solution, to ensure uniform penetration and bond inside the fibre. [4]

1.3.1 Dyes for Textile fibres

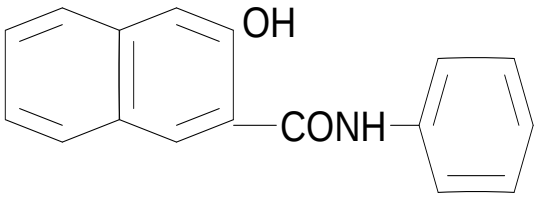
The types and structure of dyes are illustrated below and their selected fibres in which the dyes can be used:



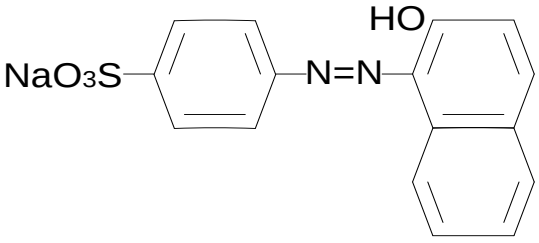
C.I. Direct Red 81 (class A): Dyes for cellulose soluble dyes, low washing fastness, and homogenous range, tinctorially strong. Wet fastnesses can be improved by after treatment. Bonded with weak bonds to fiber resulting in poor wet fastnesses.[4]



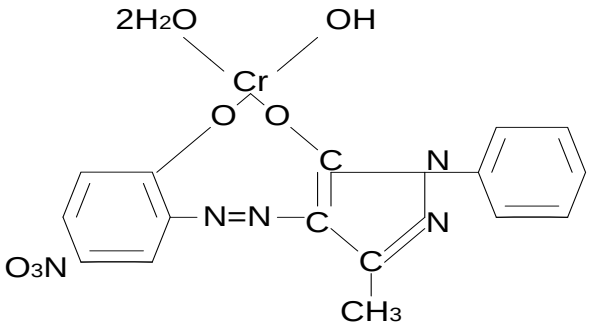
C.I. Vat Orange 9 (C.I.59700): Dyes for cellulose, the highest wet- and light fastness (7 to 8) on CEL-fiber. The resulting insoluble pigment finally dispersed inside of fiber = resist against boiling water and alkaline hot washing baths. [4]



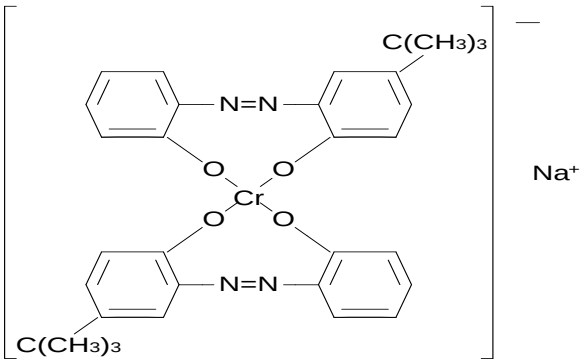
C.I. Azoic coupling component 2 (C.I37505): These are used in the colouration of cellulosic fibres, the colour is generated inside the fibre result to high fastness properties. These are seldom used in the modern, dyeing with Azoic dyes requires great care to obtain desired shades. [4]



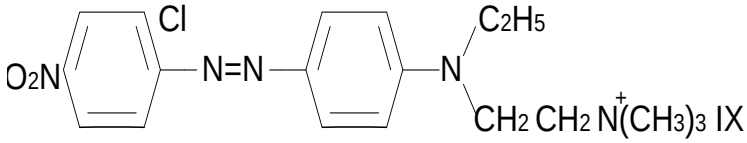
C.I. Acid orange 7 (C.I.15510): These are used for the colouration of protein fibers (wool) and nylons. They are controlled by the pH of the bath; these are applied under acidic conditions. [4]



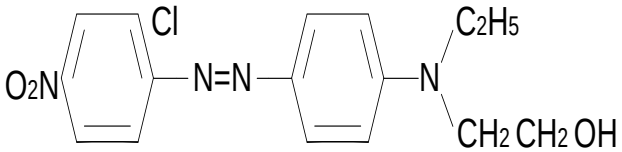
An acid dye, 1:1 metal complex dye C.I. Acid Orange 74 (C.I. 18745)



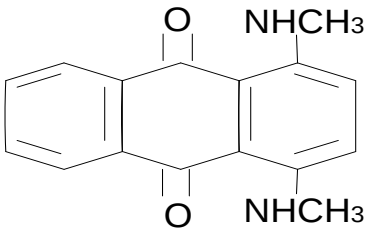
1:2 metal complex dyes: This dye is used for dyeing protein and nylon fibre; it is applied using a neutral dyebath. Both of these complex dyes require a chelating centre, which are often dihydroxyazo groups, 1:1 metal complex dyes are sulphonated, but 1:2 metal complex dyes are not sulphonated. These have high wet fastness properties. [4]



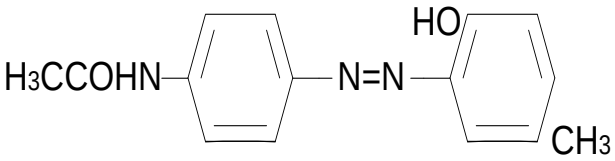
C.I. Basic Red 18 (C.I. 11085): These are used for acrylic fibers; they are cation as indicated by the + on top of N. [4]



C.I. Disperse Red 14 (C.I.11115): These dyes reproduce with the high light fastness on polyester fibres, also even higher lightness fastness can be obtained on acetate fibres and very poor lightness properties nylon.[4]



C.I. Disperse Bleu 14 (C.I.61500):



C.I. Disperse Yellow 3 (C.I.11855): The above dyes are used for polyester and triacetate fibres, one or more polar groups must be present e.g. NH_2, OH and NHR, there should be no ionic groups and the dye molecule must be planer**.** [4]

1.3.2 Fabre bonds with dye molecules

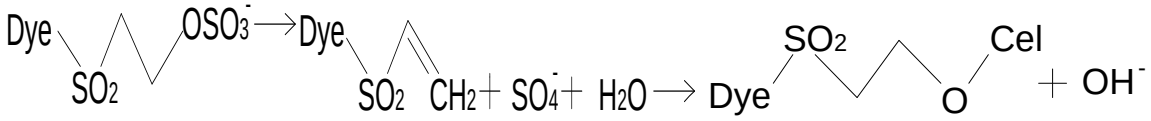
The reactions between dyes and fibers occur with some molecular force between the two being created or formed. These intermolecular attractions results to bonds being formed, the types of bond depend on the fibre and dye constituents and structures. The types of dye fibre bonds are discussed below**.**

1. Covalent bonds

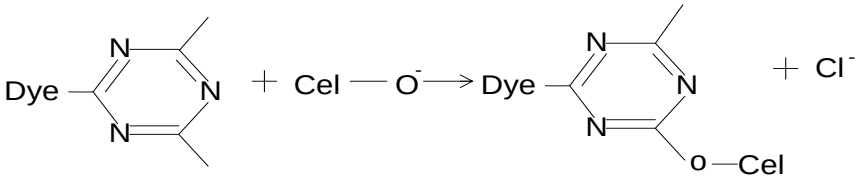
These are normal chemistry bonds which involves sharing of electrons by means of valence. The atoms involved each contributes one electron to be shared in the created common linkages which unites the atoms by forming a covalent bond of 840 kJ.Mole-1. The bonds which occur in reactive dyes and cellulose fibres are of this type. Their high energy makes them difficult to break; as a result they are highly accountable for the high fastness of reactive dyes in wet processes.[6] The covalent bonds between reactive dyes and fibres can be created either by necleophilic addition of necleophilic substitution as shown below:

$$Cel\text{-}OH + OH^- \rightarrow Cel\text{-}O^- + H_2O$$

This is a reaction for the creation of alkaline medium in order for the necleophilic reactions of dyes to occur.



***Necleophilic addition*:** The dyes used above react by nucleophilic addition, this are predominantly vinylsulphone based. The vinylsulphone reactive group is the most successful group that uses nucleophilic mechanism of the reaction.



Necleophilic substitution: The dyes reacting by nucleophilic substitution contain usually halogen atom(s) attached to a chemical structure in such way that a reaction between activated hydroxyl group and halogen atom(s) is taking place.

2. Ionic Bonds

These types of bonds occur when two atoms share a pair of bonding electrons but one can exert a preponderant attraction for both electrons. These type of are usually observed in the dyeing of protein fibers and some man –made fibers. In general all covalent bonds are partly ionic, it depends in the nature of two link atoms, this can be observed in the drawing of electronic structures of bonded atoms it can be seen that, one of these has both bonding electrons on one atom.[4] For the best illustration of these fiber-dye bonds, the acrylic fibers are selected and briefly discussed below.[3,4]

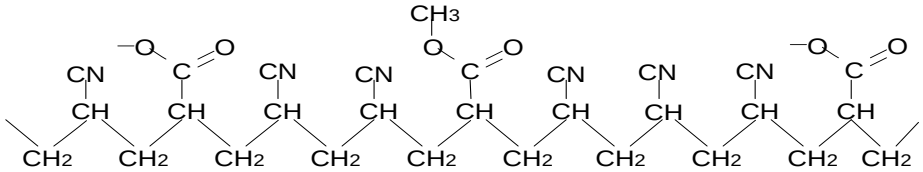


Figure 1.3.1: *Chemical structure of an acrylic fiber with two co monomers, acrylic acid and methyl acrylate.*

The presence of acidic groups allows the acrylic fibers to be dyed using basic/cationic dyes as well as disperse dyes used for other synthetic fibers can be used, resulting to light shades only.

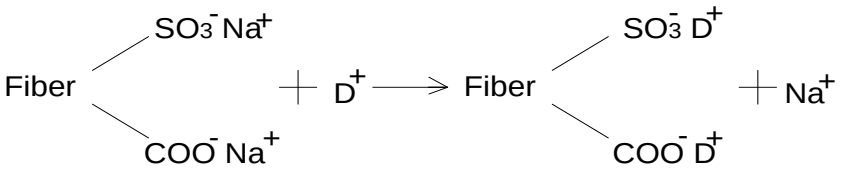


Figure 1.3.2*: Dyeing with basic dyes by means of ion exchange mechanisms*.

The D^+ for dyes has a higher affinity than the Na^+ or H^+ cations which link to the anionic group of the fiber, as a result these are displaced by the D^+ dyes. This ionic exchange occurs when the dye molecule penetrates the fiber interior; with acrylic fibers the dye molecule can only penetrate the fiber at high temperatures above the Tg of the fiber.[5,6]

3. Hydrogen bonds

Hydrogen has a very small ion, proton but with a high polarizing power, because under certain conditions it can form a bonds with two atoms simultaneously. This condition required is that the Hydrogen atom must be covalently bound to one of high electron affinity, where it is positively polarized. This occurs mainly with Hydrogen atom being bound to N, O or F, and in some cases being bound to Cl, S or C. [4] The hydrogen bond is not so strong, its about 8.4-41 kJ. $Mole^{-1}$, it can be readily made and easily broken. It can be formed by partial proton donating and acceptance.

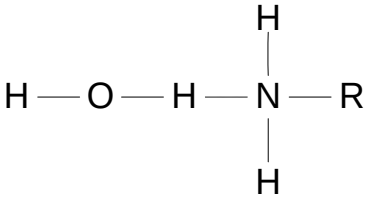


Figure 1.3.3: *Hydrogen bonds in organic compounds*

Due to this hydrogen property, Valko, Morten, Rose and other scholars reached the conclusion that, between the molecules of dye and cellulose, a union is established by Hydrogen bonds, as illustrated below. Rose subdivided the dyes into two groups, according to their electronic behavior.[3,4]

a) Groups of dyes which give electrons doublets called electron donators.

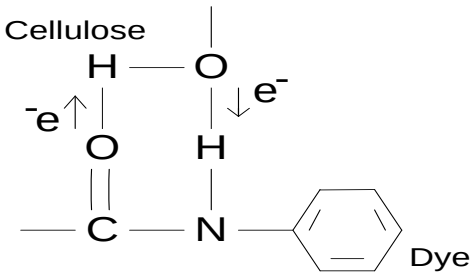
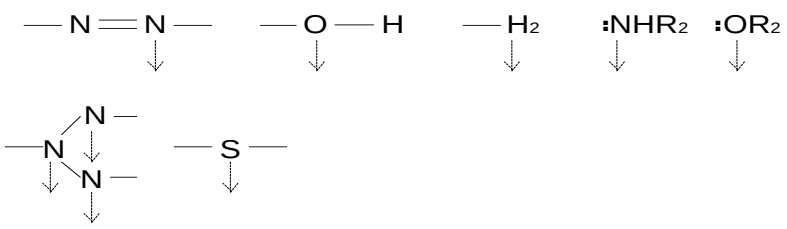


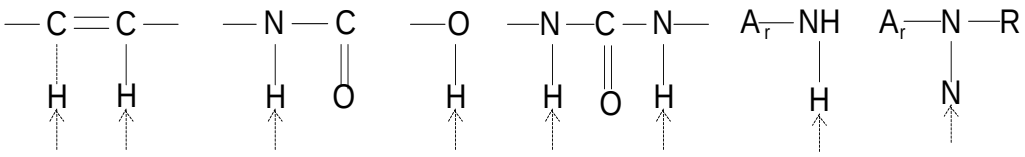
Figure 1.3.4*: Bonding by means of Hydrogen bonds between cellulosic fibers and direct dye.[5,6]*

b) Groups of dyes having hydrogen atoms, as a result they are able to form hydrogen bonds with other groups:

Group I



Group II

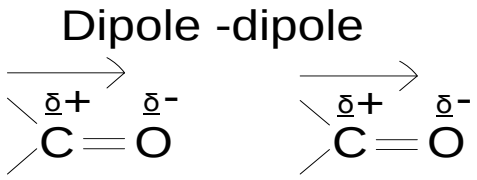


The dyes belonging to Group I; unite to the cellulose by means of the hydrogen present in the hydroxyl group, while those in the Group II, are linked by means of the oxygen atom in the hydroxyl group.[3,4]

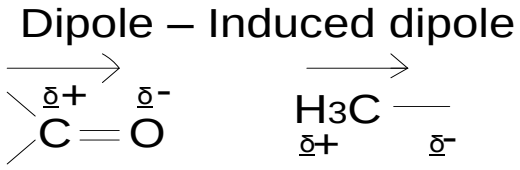
4. Van der Waals

These are weak forces between fibres and dyes, these can be divided into two main groups, known respectively as polarised (electrostatic) and dispersion forces. Sometime a term is used that includes hydrogen bonds, dipole- dipole, dipole induced dipole and pi orbital forces. [4]

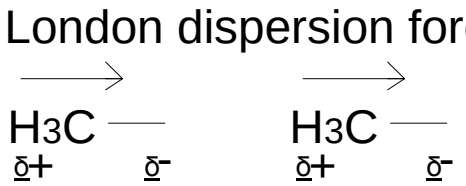
Dipole-dipole: Interaction, they originate in non homogenous distribution of electrons in permanent dipole molecules. Their energy is about 1.2-12kJ.mole^{-1}



Dipole-Induced dipole: Interactions, these come about due to polarization of neutral molecules. Their energy it's about 0.8 kJ.mole^{-1}



London dispersion forces: Interactions, these occur due to mutual polarization of neutral molecules. Their energy is about 0.1 kJ.mole^{-1}. These are very weak interactions.



1.4 DYEING TECHNIQUES

1.4.1 Swelling of fibres and Plasticisation

Most dyers believe that for hydrophilic fibres, they must swell first in the dyebath before the dyeing mechanism can take place. They also believe that plasticisation of fibres goes hand in hand with the swelling effect. These two mentioned phenomena are said to occur, when the Tg of fibres is lowered/reduced by some dyebath additive or water. After some careful observation by some scholars, it was concluded that swelling and plastisation does not go hand in hand, because some of the dyebath additives increases the swelling at the same time also increasing the Tg of fibres. [4]

1.4.2 Practical Dyeing Systems

1. Solvent dyeing: Over the years there has been a great improvement in solvent dyeing due to the water medium being replaced by other organic solvents in the transportation of dyes. The

most successful first method of solvent dyeing is the dyeing of polyester and nylon knitted fabrics with perchloroethylene as a dyeing medium (solvent). The various chemical and physical requirements/fundamentals of solvent dyeing are discussed below.

The Choice of the solvent

The solvent for dyeing must be readily available and inexpensive, readily recoverable and non-toxic and non-flammable. It should be chemical stable to textiles as well as the equipment and conditions under which it is used. Many years treated water has been used as the solvent for textile processing, but developments has been done in this field to improve dyeability of fibers by use of different solvents such as Tetrachloroethylene.[4]

The different between tetrachloroethylene solvent and water in the dyeing mechanisms is that; water is a polar amphiprotic substance with a defined pH values, a high dielectric constant, a high dipole moment, and a structure which can lead to hydrophobic interactions. The tetrachloroethylene is a non-polar solvent with no pH values and it has completely different properties compared to water. [4]

2. Solvent assisted dyeing: Water soluble substances are used as additives to assist in the dyeing system. These were firstly observed in the dyeing of wool and silk fibres; the water soluble additives such as benzyl alcohol or various amines are incorporated in the neutral dyebath with a selected milling/metal complex dyes, as a result the dyeing times are shortened because of these additives used to assist in the dyeing process. The solvent assisted technique is also used for man-made fibres. [4]

3. Carrier dyeing: This technique is generally used for polyester dyeing because the fibre is hydrophobic and the disperse dyes for polyester are have a very low solubility in water. Studies have been done to try and explain the mechanisms or the effects of carriers in the in the dyeing system of polyester fibres. Zimmerman *et al.* [4] claims that in the presence of the carriers, there is more disperse dye existence in the solution as a result there is more dye readily available to diffuse inside the fibre.

Balmforth *et al.* States that the carrier mechanisms has to functions on the dyebth, the first one is that the carriers increase the equilibrium uptake of dyes and a rate of dyeing, whilst the other function is that they solely increase the rate of dyeing. [4] During the carrier dyeing process there is evidence that to aspects occur to the fiber, which are fiber swelling and plasticisation.

4. Pigment dyeing: Pigment dyeing is carried out using water insoluble dye pigments. This process is carried out for highly non hydrophobic fibers, such as polypropylene, arimid fibres, glass fibres etc. These can be dyed during the yarn formation (spinning) stage by addition of

coloured pigments to obtain a required colour. During this process the polymer chips are melted using high temperatures followed by addition of coloured pigments. During this process levelness is also required and must be maintained throughout the whole batch.

1.5 COLOURATION OF TECHNICAL FIBERS

Application of colorants to technical textile (high performance fibres) is a complex field because of the variety of fibres, filaments, yarns, fabrics and other materials requiring coloration and the diverse nature of the end-use and performance requirements. Coloration may be carried out by dyeing the materials to a uniform colour, or by printing to impart a design or motif to the technical textile. Fibres, yarns and fabrics may also be multicoloured by specialised dyeing techniques, for example space dyeing, or by weaving or knitting different coloured yarns. The colorants used can be selected according to the type of fibre to be dyed and the end-uses; these may be either water-soluble/slightly water soluble dyes, it's also possible to use water insoluble pigments. These may be applied in aqueous medium in dyeing and in printing; some can be dyed in supercritical fluid carbon dioxide under very high pressure.

Dyeing is normally carried out on textile materials from which surface impurities, for example fibre lubricants, spin finishes, sizes, particulate dirt or natural colouring matters and so on, have been removed by appropriate pre-treatment such as desizing and scouring and to which a stable whiteness has been imparted by chemical bleaching. However, many synthetic fibres do not normally require chemical bleaching prior to coloration because the fibres may be whitened by incorporation of a fluorescent brightening agent during fibre manufacture.

Printing may be carried out mainly on technical fabrics that may be in their natural state, or chemically bleached, or whitened with a fluorescent brightening agent, or after tinting or dyeing. Conventional dyeing and particularly printing are most conveniently and economically carried out on fabrics, which also allow greater flexibility through the selection of colours late in the technical textile production sequence to meet the varying market requirements.

2. TEXTILE FIBERS

2.1 TEXTILE FIBERS IN GENERAL

There are certain criteria that a natural or synthesised polymer must meet to be classified as a textile fibre material. The material has to have certain required properties which are usually achieved by either two following factors.

a. Chemical composition: It is of great importance especially in the wet processing stage of the fibre material for textiles.

b. Technology of Production: Fibres of both natural and man made have to undergo certain production stages starting with obtaining the initial fibrous material to spinning and weaving of the fabric. The properties of the fibres are greatly changed through out the production stages of the fibre.

2.1.1 Fibre Properties

- Geometrical properties: Length, fineness and shape of the fibre cross section.
- Mechanical properties: Strength, break elongation, modulus, stiffness, recovery
- Mechanical and thermo mechanical properties: Melting point, thermal resistant, transition temperatures, loss angle and loss modulus
- Electrical properties: Static charge, dielectric behaviour, tribology, insulation and conductivity.
- Abrasion and aging: Chemical resistance, weather resistance, flame resistance etc.

In textile manufacture there is a wide range of textile fibres which can be used for different end uses such as apparel, automotives, carpentry, geotextiles etc. Depending on properties of the fibre and the dyeability/finishing capabilities are the fibres selected for the final product. Textile fibres can be classified in these categories:

1. Cellulosic fibres
2. Protein fibres
3. regenerated man made fibres and
4. synthetic fibres including high performance fibres

2.2 CONVETIONAL HIGH PERFORMANCE FIBERS

Natural fibres such as cotton, flax, jute and sisal have been used for centuries (and still are used) in applications ranging from tents and tarpaulins to ropes, sailcloth and sacking. There is evidence of woven fabrics and meshes being used in Roman times and before to stabilise marshy ground for road building – early examples of what would now be termed geotextiles and geogrids. These fibres above have not too much significance to this study because they are natural fibres, their dyeing mechanism does not involve same procedures as that of synthetic fibres, and there are similarities yes but they can not be used to explain and compare them with the dyeing mechanism of synthetic high performance fibres. [5]

2.3 HIGH PERFORMANCE FIBERS

In the last half-century, a new generation of high performance fibres were developed which were high-modulus and high tenacity fibres, these contributed in strength and stiffness. These fibres have a high thermal or chemical resistance, they were negative contributors in clothing and apparel fabrics but they play a major role in technical requirements where comfort and fashion is not of great importance. Some of these high performance fibres will be discussed lengthily in these study mainly their dyeabilty properties. High performance fibres are difficult to dye, especial in solvent dyeing because of their glassy surfaces due to their chemical molecular structure and the arrangements of polymers within the structure.

2.3.1 Aramide Fibres

Aromatic polyamides became breakthrough materials in commercial applications as early as the 1960s, with the market launch of the meta-aramid fibre Nomex by DuPont, which opened up new horizons in the field of thermal and electrical insulation. A much higher tenacity and modulus fibre was developed and commercialised, also by DuPont, under the trade name Kevlar in 1971. Their outstanding potential derived mostly from the anisotropy of their superimposed substructures presenting pleated, crystalline, fibrillar and skin-core characteristics. [5]

Another para-aramid, Twaron similar to Kevlar, and an aromatic copolyamide, appeared on the market towards the end of the 1980s. The aromatic copolyamide derived from a good fundamental understanding of the earlier work done with rather stiff para-aramid chains and the new space created for more flexible, high tenacity fibres. Teijin, after a remarkable scientific interpretation of the prior art by Ozawa and Matsuda, who pioneered the development of the aromatic copolyamide fibre, commercialised the Technora fibre. [5]

2.3.1.1 Polymer preparation

Aramid a manufactured fibre in which the fibre-forming substance is a long chain synthetic polyamide in which at least 85% of the amide (—CO—NH—) linkages are attached directly to two aromatic rings. Aramids are prepared by the generic reaction between an amine group and

a carboxylic acid halide group. Simple AB homopolymers may be synthesised according to the scheme below:

$$n\text{NH}-\text{Ar}-\text{COCl} \rightarrow -\ [-\text{NH}-\text{Ar}-\text{CO}]-n+\text{HCl}$$
$$\text{A} \qquad \text{B}$$

A similar reaction scheme also yields AABB homopolymers, and these reactions can be done using several methods, such as such as interfacial polymerisation and low-temperature polycondensation, which remains the most frequently, encountered synthesis. Melt or vapour-phase polymerisation reactions should also be mentioned. The early AABB polymers contained predominantly meta-orientated linkages. These were produced by DuPont in the manufacture of Nomex fiber. With the following chemical formular:

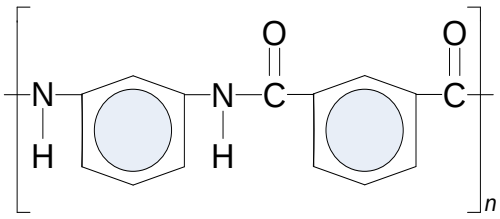


Figure 2.1: *Nomex fibers with the meta-orientated linkages*.

The high modulus, high tenacity fibres from liquid crystalline solutions of synthetic para-aromatic polyamides led to the commercial production of Kevlar aramid fibre; the corresponding chemical formula is given below:

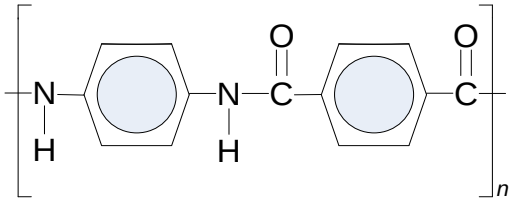


Figure 2.2: *Kevlar fibres are poly (p-phenylene terephthalamide) (PPTA) the simplest form of AABB para-orientated polyamide. [5]*

2.3.1.2 Aromatic polyamide polymerisation process

Aromatic polyamides of the PPTA type are usually synthesised via a low-temperature polycondensation reaction based on *p*-phenylene diamine (PPD) and terephthaloyl chloride (TCl), according to the following reaction:

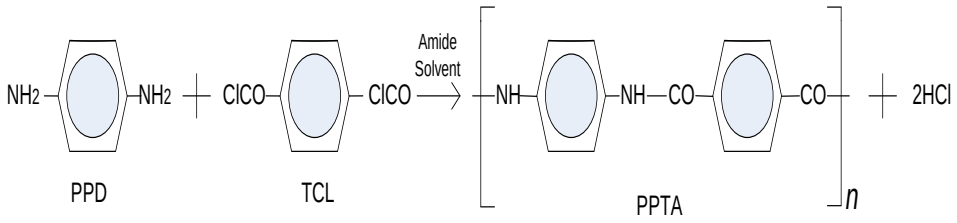


Figure 2.3*: Polycondensation reaction of PPD+TCL=PPTA*

One methodology involves the dissolution of appropriate quantities of PPD in a mixture of hexamethylphosphoramide (HMPA) and *N*methylpyrrolidone (NMP), cooling in an ice/acetone bath to 258 K (-15°C) in a nitrogen atmosphere, and then adding TCl accompanied by rapid stirring. The resulting product is a thick, paste-like gel. Stirring is discontinued and the reaction mixture is allowed to stand overnight with gradual warming to room temperature. Work-up of the reaction mixture is accomplished by agitating it with water in a blender to wash away solvent and HCl. The polymer is collected by filtration. [5] The polymer chips are spun to yarns using high temperatures, the cross-section of the filament will depend on the shape of the spinnerets.

2.3.1.3 Colouration of Aramide Fibers

The polymer chains of aramide fibers are highly oriented, resulting to crystalline chains within a structure with high melting points of about 500 ^{o}C. The Tg of these fibers is also high as a result it is very difficult for the dyestuffs to penetrate the fiber and yield suitable variety of shades at required fastnesses. By looking at the structure ***Figure 2.4*** below, it can be seen that the structure of (Kevlar) aramide is sold and the polymer chains are linked by hydrogen bonds.

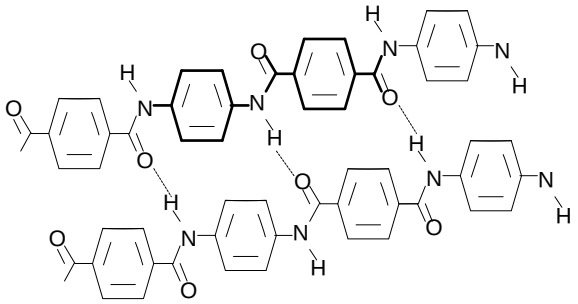


Figure 2.4**:** *Arrangement of polymer chains in the structure of Kevlar fibres linked by hydrogen bonds.*

The strength of the material comes from the high degree of bonding within the molecules of the chains and the hydrogen bonding between the two/more chains. The obvious and the only logical way to obtain a good fibre bond would be to interrupt the hydrogen bonds which join the two polymer chains together. The placement of N-H and C=O groups in the structure are

similar to that of nylon fibers as a result it's possible to use these dyestuffs, acid dyes, disperse dyes, basic/cationic dyes. The methods and techniques of dyeing aramids are discussed below. [6]

Problems in the dyeing of aramid

(a) The dyes have to be attached to the fibre molecules, as a result that is possible only by breaking the hydrogen bonds which keeps the polymer chains of the fibre linked together. If hydrogen bonds are broken the strength of the fibre decreases.
(b) Another problem about aramide fibres is the difficulty in wetting out the fibre. Suggestions have been made to use carbon dioxide under pressure instead of normal dyeing medium.
(c) Difficulties in the colouration of aramide blends to suitable uniform colours, especially blends involving Kevlar and Nomex.
(d) Many used dyeing additives result mostly in the decrease of fibre strength compared to untreated/greige fabrics.

(a) Carrier dyeing of aramid fibers

This method of dyeing comprises of a mixture of a carrier and a dye soluble or dispersible in the carrier. The selected carrier is the N-cyclohexyl-2-pyrrolidone and methyl benzoate, it was determined that this carrier was not only suitable for Kevlar dyeing only; it's also suitable for the dyeing of Kevlar blends with other polymer fibers. This method of dyeing can be carried out for woven/knitted fabrics, yarn dyeing, sliver etc, and there is no need for special equipment the conventional dyeing mentions are suitable for this process. The total weight of the carrier in the fibre is about 1-3% on the weight of the fiber and the carrier can also carry other additives such as retardants, softeners, UV absorbers etc. [7]

In practice the dyeing is carried out in the one step batch process at 100 ^{0}F – 300^{0}F at 1-3 atmospheric pressure. The fabric can be dyed by a normal jet dye machine or any other pressurised dyeing machine available. [7]

(b) Supercritical carbon dioxide

The use of supercritical carbon dioxide is emerging as a potential method for achieving pollution-free dyeing. An important factor in supercritical fluid dyeing is the solubility of the dye in supercritical carbon dioxide. Measurements show that the solubility of C. I. Disperse Red-60 dye in supercritical carbon dioxide is significantly enhanced upon addition of polar cosolvents : ethanol and acetone. The solubility enhancement is attributed to the formation of hydrogen bonds between cosolvent and dye molecules. Observed solubility behavior is correlated using dilute-solution theory with lattice-fluid-hydrogen-bonding model. [8]

The solubility of dye can be easily controlled by temperature and pressure, in addition the SFD gives better dyeing results due to high diffusion of the dye through the fluid solution to the fiber and also the CO_2 solution swells the fiber creating easy wettability and penetration of dye into the fiber. Also the CO_2 does not only break form hydrogen bonds with the dyestuff only, the hydrogen bonds inside the aramide fibers are broken by the CO_2 and new dye-fiber bonds are created. [10] Another major aadvantage of using SFD is that the dye can be recovered easily from waste effluents result to the decrease in water pollution and there is no washing and drying steps required.

(c)A pretreatment method for dyeing aramide fibers

According to S.K. Obendorf and V. Ravichandran a pretreatment method for dyeing Kevlar fibers without dye carriers has been developed. Fibers were metalated by reacting with a methylsulfinyl anion, the metalated fibers were dyed with cationic and direct dyes, and the resulting coloration and physical properties were evaluated. The results show that this pretreatment technique can improve the dyeability of Kevlar without compromising mechanical properties. Metal cation improved dyeability more than grafting with either adipoyl chloride, benzoyl chloride, or vinyl benzyl chloride.[9] According to Davis et al, it is highly advisable to pre-treatment the aramid fibers with a flame resistance finish before dyeing rather then as an after treatment. This has been discovered that, the dyeing properties of the aramide fibers are improved greatly, this is said to be due to the fiber swelling effect of the process. [10]

The swelling agent system is composed of at least two components; an organic polar solvent, and compatible, miscible diluents which do not participate in the dyeing reaction to minimise the fiber damage. The suitable swelling agents are selected from dimethylsulfoxide, dimethylacetamide and N-methylpyrrolidone. [10] The diluents may be water, xylene, dimethylbenzene etc. This process is carried out in aqueous solutions at water ratios of 90:10 (DMSO) using the pad-oven-dry continuous process. [10]

2.3.2 Polypropylene

These fibers were discovered by just before 1957 *Natta,* transferred the polymerization process by *Ziegler* onto polypropylene. Of its four stereo specific modifications only the isotactic polypropylene with a melting point of 162... 176 ^{0}C was suited for fiber production. These were not used up until 1980s after a long research and development made PP much later a textile material with remarkable properties at low cost, that since 1980 continuously gained relevance as the fourth synthetic fiber class next to PA, PET and PAN textiles.[11]

2.3.2.1 Production of Polypropylene

Propylene is a liquiefiable unsaturated carbonhydroxid in gas form resulting from the refinery of crude oil/petroleum with SP = —47 0C that can be produced by two processes: either as a

combined product with ethylene and as a higher carbonhydroxides during the high temperature pyrolisis of the petroleum distillation and natural gas fractionating or as a byproduct of gasoline duringhydrolytic cracking of higher carbonhydroxides. The latter is the more frequently used process; to obtain spinnable PP it is necessary for the propylene to be of > 99.5% purity, for molded parts production only 93% purity is sufficient. It can be polymerized into isotactic configuration that is achieved with the help of Ziegler-Natta catalysts; today catalyst systems of the third generation are used that provide a higher selectivity for isotactic PP and a higher yield. [11]

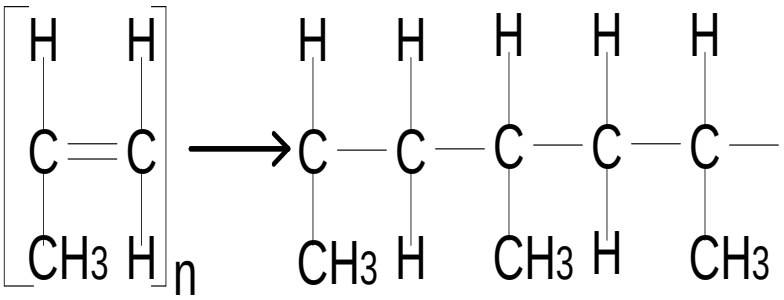


Figure 2.5: *The transition from propylene to polypropylene occurs according to this formular*

2.3.2.2 Dyeing of Polypropylene fibres

Poplypropylene can not be dyed in traditional ways of textile dyeing. During dyeing of textiles the fibres are swelled by water allowing the dyestuff to enter the fibres' and form bonds with the molecules of the fibres but in the case of polypropylene, the hydrocarbon composition of the fibre does not swell by the water, as a result there is little penetration of dye to the fibre. The dye is removed from the surface by abrasion or mechanical use of the fibre during pilling. The same problems experienced in the normal dyeing of the above mentioned aramids can also be experienced with the colouration of polypropylene fibres.

(a) Creation of dye site during the spinning process

Dyestuffs need to be added into the melts as organic and inorganic pigments just like dulling and optical brighteners. This process has been done using dye receptors with low molecular weight such as salts, alcohols, acids and amines to create sites for dye bonding. The additives used must be compatible with the fibre in terms of melting temperatures, and must be able to produce fine dispersions within a fibre. These are difficult to control because of the lack of migration properties within the fibre and they usually produce dull colours. Many methods have been tried which are expensive and some do not produce positive results. The whole aim of these methods was to modify the fibre before dyeing so that there can be bond creation between the dye and the fibre molecules.

(b) Carrier Dyeing of Polypropylene

In this case there is no modification of the fibre polymer prior to dyeing; the fibres are contacted with the colloidal emulsion, this is at/above the Tg transition temperature of the polypropylene fibre. The emulsion is prepared by mixing water with a long chain alkyl substituted anthraquinone dye dissolved in organic solvent. The dye has been found to penetrate the fibre and be distributed evenly producing suitable colour yields. The anthraquinone dye must have 18 carbons in its molecular chain to be more effective for the dyeing of plypropylene. The dyebath is heated to about 90^0C. [12]

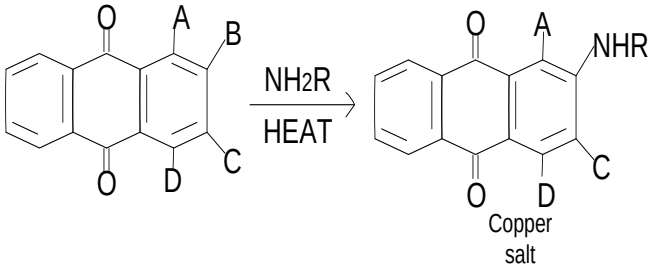


Figure 2.6: *Synthesis of the anthraquinone dyes*

This is a Group IV class of dyes, called Beta-amino anthraquinone dyes, generated by at least a beta-halogen, -hydroxyl, or a sulfonate substituted anthraquinone and a long chain branched alkyl amines, these have a the same color as the beta-amino antraquinone material since the beta position does not contribute to the color of the dye. [12]

The preferred emulsifiers are aromatic and aliphatic hydrocarbons, esters, fatty and other organic acids, triglycerides, amides, imides, non-ionic polymers, anionic and cationic polymers, alcohols and ethylated derivatives of these. The dyes are 0.1-25% of the wait of the fiber and the solvent is about 0.5-50% of the wait of the fiber, depending on the depth of the desired shade. While dyeing the temperature is about 212^0F being raised 5^0F per minute and held for 30-60minutes the resultant fiber had uniform dye distribution and fast to light and washing.

(c) Supercritical Carbon Dioxide Dyeings

The following experiments of dyeing polypropylene fibres using supercritical Carbon dioxide were conducted by Jae-Jin Shim et al at the School of Chemical Engineering and Technology, Yeungnam University in Korea. Disperse R60 dyestuff was used in A closed-loop high-pressure sorption apparatus (batch-type) circulated by a magnetic pump was placed in a constant temperature air bath controlled within ±1 K. The dyeing parameters used were 120^0C temperature and the pressure was 10.1-30.4 MPa with no special co solvent added in the dyeing vessel. [13]

The amount of dye sorption in polymers in the presence of supercritical carbon dioxide is closely related to both the solubility of dye in the fluids and the distribution of dye between the fluid and the polymer phases. The mobility of dye molecules between polymer chains is generally enhanced due to the swelling of polymers in the supercritical fluids. At high pressures the increasing rate was slowed down, indicating the polymer was almost saturated with the dye molecules, at pressures lower than 5 MPa. [13]

The higher the temperatures used the higher was the dyestuff diffusion to the fibre due to the increase solubility of the dyes through the supercritical carbon dioxide fluids. The results showed that the polypropylene fibres which are colored by this method had high wet fastness properties. It was also discovered that addition of co solvents in supercritical dyeing of polypropylene increased the dye adsorption to the fiber resulting to deeper shades.

2.3.3 Glass fibers

Fiber glass was invented in 1938 by Russell Games Slayter of Owens-Corning as a material to be used as insulation. During WWII when shortages of strategic materials forced manufacturers to seek alternate materials, fiberglass was combined with resin to create the first modern composites. Glass fiber is an amorphous material that consists of a silica (SiO_2) backbone with various oxide components to give specific compositions and properties. Several types of glass fibers are manufactured but only four are used in composites: E-glass, S-glass, C-glass and quartz. E-glass has a calcium aluminorosilicate composition with maximum alkali content of 2%. They are originally used when strength and high electrical resistivity were required. E-glass fibers are used in various electrical devises. Because of their good strength properties and low cost, E-glass fibers are the most common type of fiber glass used in composites. [14]

2.3.3.1 Manufacture of glass fibers

All glass fibres are silica based **SiO2 + complements.**
Mostly used complements for glass melts are oxides of Ca, B, Fe, Al, Mg, and fibres are drawn of particular oxides melt enriched by small amount of alkali metal oxides (Na, K) and glass fibres are classified according to particular oxides mixture.

The raw materials of glass fibers are silica and various subcomponents such as limestone and boric acid and some minor ingredients such as clay, coal and fluorspar. These are dry mixed and melted in a high temperature refractory furnace. The temperature of this melt varies for each glass composition, but is generally about 1260°C. Two similar processes are used for the manufacture of glass fibers from the molten mixtures of sand and the subcomponents. These processes are called the marble process and the direct-melt process. After the glass is melted marbles are formed which allow for ease of transport of the glass and the subsequent reheating

in the latter part. The direct melt process simply removes the marble formation and couples the melt chamber directly to the filament formation stage. [14]

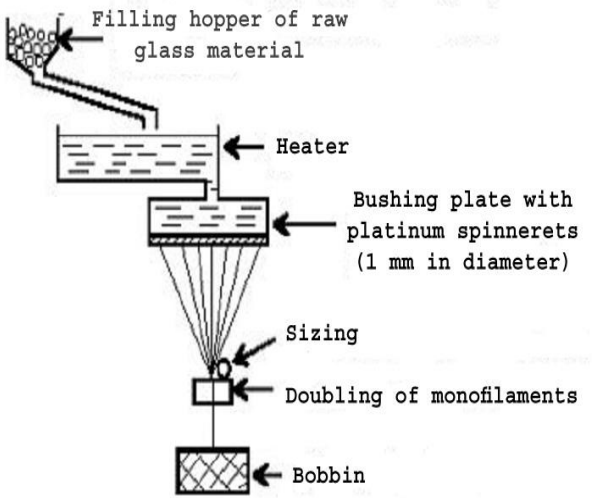


Figure 2.7: *Manufacturing schematic diagram of glass fibers.*

The fibers are formed by directing the melt into the formation bushings, which are low-corrosion metal such as platinum plates that have a multiplicity of tiny holes, typically 200 – 1200 holes. The molten glass flows through the bushing holes and forms continuous strands called filaments. Then the filaments are cooled or quenched by spraying with water or simply air. Thereafter they are gathered together. The diameter of the fibers is controlled by the hole size in the bushing, the temperature, viscosity of the melt and the cooling rate and method. [14]

2.3.3.2 Dyeing of glass fibers

The glass fibers have many good properties they are applied extensively in many facilities and in materials such as fiber-reinforced plastics. However, glass fibers cannot be dyed easily and satisfy optical sensitivity, due to the compositions of the glass fibers containing far less hydroxyl groups on the surface.[15] The less hydroxyl groups on the fiber surface can not be bonded strongly with the dyes, resulting to poor color fastnesses. Suitable methods of dyeing glass fibres have been invented over the years, some of these are discussed below.

Problems associated with dyeing of glass fibers
1. Decrease of strength
2. Decrease of fire resistance
3. Fabric hand stiffer and harder for woven and knits

a)Methods of improving colouration of glass fibres

Many researches have been done based on this top as far back as the 70s, but there are always drawbacks to the previous inventions of improving colouration of glass fibres. The mojor drawbacks are the decrease of strength of glass fibres, decrease of fire resistance, and notabily the fabric hand, the knitted or woven fabrics become stiffer and harder after being treated with treatments to improve colouration processes with suitable colour fastnesses. The most recent method has been invented by the Japanese, Kozo Maeda and Masakazu Date; this invention comprises of treating glass fibres with an aqueous solution combination of sulfer-oxygen containing acid or peroxy acid/water soluble salt and then followed by inorganic or organic water soluble salt and then dyeing with a basic dye. [16]

This above treatment also serves as the desizing process of glass fibres, at the same time it increases the basic dye affinity for the glass fibres. It is suitable for all forms of dyeing resulting to high dye fastnesses and a suitable fabric hand, at has been noticed also that there is no decrease in fabric strength.

Assumptions have been made by observing the exhaustion of basic dyes by treated glass fibres, that an anionic radical such as SO_x is introduced into the glass fibres through a react ion of glass fibres with an acid, resulting to the anionic radical functioning as a dye site to which the basic dye can adhere. [16] Another assumption is that the proxy acids or water-soluble salts may form an aqueous solution which is an ionic radical by the following equation:
$S_2O_n^- \rightarrow 2SO_4^-$ this radical can be join to a silanol radical or –O-Si-OH, this radical is a hydrate of the main ingredient of the glass fibres, which is located on the surface of the glass fibres and is also the dye sites where the basic dyes can adhere.[17] Its is also noted that a compound such as methyl sulphate or sodium pyrosulphate can be used for this purpose, which can form the corresponding sulphur-oxygen acid or the acid salt thereof by thermal decomposition or hydrolysis during the treatment of such compounds by means of the following equations:

$2\ CH_3\ HSO_4 \rightarrow (CH_3)_3\ SO_4 + H_2SO_4$
$Na_2S_2O_3 + H_2O \rightarrow 2\ NaHSO_4$

The sulphur-oxygen containing acid or peroxy acid/water-soluble salts may be used alone or in combination. The amounts of these compounds are usually from about 0.1 to 10%, preferable from about 0.3 to 2% of the weight of the treated solution. When smaller amounts are used compared with the lower limit, there would be no improvement in the dyebilty of the fibres, and when higher amounts are used more than the upper limit; there will be a significant damage to the fibres.

b) Methods of dyeing a glass substrate with a polycationic dyestuff

Many methods have solutions have been developed and proposed for colouring of glass substrate; such as surface coating with coloured dyeings and basic dyeing after pretreating with sulphur-oxygen or peroxy acid; and dyeings of the molten mass with inorganic pigments. It has

now been found that a glass substrate can readily be dyed with polycationic dyestuff in the absence of any sizing agent. Polycationic dyestuffs are dyestuffs having at least 1.3 cationic groups per dye molecule, whereby a non-integral number of cationic groups are to be understood as an average value for the molecules of the dyestuff in question.[18]

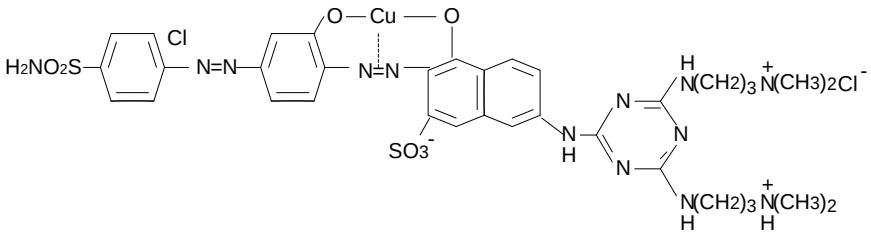


Figure 2.8: *phthalocyanine dyestuff containing cationic groups*

The dyestuff may also contain anionic groups, particularly sulphonic acid groups, but if any such groups are present, then the number of cationic groups per mole must be at least one greater than the number of anionic groups per mole. [18]

The dyes maybe metallized or metal free, but metal complex dyes are preferred being 1:1 and 1:2 metal complex azo dyes. Azo dyes as well as other cationic dyes, for example phthalocyanine (preferable copper phthalocyanine) dyes and antraquinone dyes may be used. Dyes containing a fibre-reactive group may also be employed. The dyes have to have a free action and a molecular weight of 400-1000. The exhaustion ratio of these dyes should be about 90-100% measured on cotton substrate.

The dyeing of glass fibres according to this invention may be carried out on the number of dyeing process such as, continuous, discontinuous methods. The dyeing may be done using for example, the exhaust method e.g. with the circulation of the substrate or circulation of the liquor at a pH of 1 to 14, preferable at 3 to 7, advantageous when using temperatures of 20^0 to 150^0 C, the liquor to fabric ratio being 1:1 to 10 000:1. In case of the continuous methods it is preferably to impregnate with the dyeing liquor followed by treating with hot air or steam for exhaustion at 100-130^0 C or thermo fixation at 100-230^0 C. [18]

The invention is concerned with direct dyeing of uncoated glass fibres, which are not coated with the size or any grease. To remove such coatings, the substrate is pre-treated with hydrochloric acid preferable in 0.5-10% diluted form at 20^0-100^0 C for 60 minutes in the ratios of 1:1 or 1:1 or 10 000:1. Depending on the type of size used the substrate may be treated with formic acid, detergents and oxidant such as hydrogen peroxide.[18] Level dyeing are obtained on the glass fibres, with good light and wash fastnesses, excellent rubbing fastnesses and a high bleeding fastness, in water, alcohol and soap. No requirement of an after-treatment after the dyeing. Glass fibres dyed according to this invention are used in a large field of applications such as reinforcing plastics or textiles, non-flammable decorative articles, thermal, clothes and curtains, electrical and humidity insulations, optical glasses and light wave cables.[18]

3. EXPERIMENT PART

Laboratory experiments will be conducted as a form of data collection method, to establish new possible methods for improving the dyeing of glass fibres by selecting suitable dyestuffs and using a special solvent. Evaluations and discussions will follow there after depending on what has been observed and obtained from the laboratory experiments. The data will contain successes and failures obtained from these experiments and they will be included in this diploma work.

The dyeing process will be selected according to the types of materials which will be used to produce high fastness properties. During this work many methods and materials will be explored. The basic methods and materials are discussed below but we have to keep in mind that, they are subjected to changes as the experiments progress and results are obtained. Overall this part of study will be carried out in steps as it will be discussed below.

3.1 METHODS AND MATERIALS

The methods have to simple as possible and practically applicable in bulk dyeing in factories for production purposes with minimal difficulties and costs. Generally there will not be any special equipment for conducting laboratory work; lab dyeing will be done under normal procedures with the exception of different solvents and temperatures which will be used to obtain high dyes fastnesses to the fibres.

3.1.1 Experimental Methods

Initially 4 steps have been proposed to carry out the laboratory experiments for the dyeing of glass fibres. These will be coloured using the normal surface dyeing technique. This will involve padding the substrate with the dye solution, drying at room temperature and followed by fixation using elevated temperatures.

The laboratory experiments will be guided based on the following steps:

1. **Selection of dyestuff:** as it is widely know that there are a numbers of suitable dyestuffs classes which are used for the colouration of the special fibres which have been selected for this diploma work. It has been decided that the choice of dyes used for this work will be selected from the following 3 classes of dyes; Cationic dyes, Disperse and Metal complex dyes. These will be selected according to their solubility to a proposed type of solvent that will be used as a dyeing medium.

2. **Spectroscopy:** Calibration lines for dyestuff absorption with dye concentration will be developed for the selected dyestuff from each group/class of dyes which are mentioned

above. At the end 3 main dyes Red, Yellow and Blue must be selected for the purpose of colouration of fibres selected for this study. It is also possible that the dyes selected will be a mixture of all three selected dye classes provided they are compatible to be used together resulting to high fibre affinity and high fastness properties can be obtained.

3. **Application of TMSPM solvent:** this procedure will be conducted for the selected optical dyes. There is a lot of data which will be collected depending on the results obtained from this step.

4. **Fastnesses:** The main aim of colouration is to produce dyeing of highest fastness properties, mainly wash fastness and light fastnesses. This is a result of good dye-fibre bondage, which can be enhanced greatly by highly controlled dyeing parameters and good selection of your dyeing materials in terms of dyes, solvents and other dyeing auxiliaries which are essential to produce colours of required fastnesses.

3.1.2 Materials and Apparatus

It is necessary to use clean and calibrated laboratory equipments in order to receive accurate results to the maximum levels. Most of the materials and apparatus needed for these works are listed below some will be added as the work continues:

Materials

- Fabric samples:

  Glass filter paper

- Dyes: all the possible dyes which can be used to colour the mentioned fibers will be tested, and the ones with the best result will be used for colouration of fabric samples.

- Solvents

  1. Isopropylanol: for testing the solubility of dyes

  2. Sol preparation based on TMSPM
     The basis for the preparation of the sol was TMSPM ((3-trimethoxysilyl propyl-methacrylate).

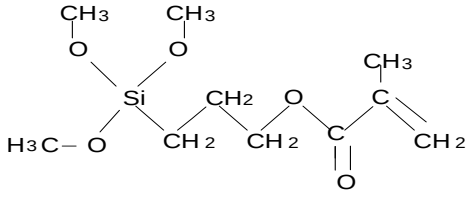


Figure 3.1: *chemical formula for TMSPM sol gel solvent*

Sol preparation principle is based on TMSPM disbandment in first half needed volume of IPA and other components (water, HCI, BPO) disbandment in second half needed volume of IPA. Then both solutions were blended with intensive mixing. Made sol was warming-up into boiling point under backward cooler for 30 minutes. After 30 minutes, sol was cooled. Part of sol was diluted with IPA in proportion to 1:4. Sol was labelled like AC4. Preparation of sol was done by one of the members at chemical institute of TUL.

The solution is as a solvent for dyeing of high thermal fibres, it has to be controlled carefully because of its quick evaporation property by doing so the dyes become less soluble in the solution and there is a possibility of dye being removed from the surface of the substrate due to this evaporation. If not in use it should be kept tightly locked and it is only stable for little number of days.

Apparatus

- Test tubes and bickers
- Graduated cylinders
- Pipettes (graduated)
- Scissors
- Fouler Mangle for padding
- Dryer for fixation
- Spectroscopy for calibration curves/lines to obtain dye concentration with absorbency
- Centrifugal machine for the segmentation of dye particles
- Weighing scale for dyes and chemicals
- Blue scale for light fastnesses
- Grey scale for wash fastnesses
- Temperature box, for testing of fastness to high temperature above 200^0C
- UV light for testing light fastnesses

3.2 EXPERIMENTS

The first experiments are to test for the solubility of the dyes, for this study three types of dye classes are selected and all available dyes of these classes in the laboratory are tests for solubility. The first step is to test using the normal visual test, whereby a small amount of dyestuff is added to the test tube followed by addition of a solvent, in our case the isopropyl alcohol is used as the solvent for testing the solubility of dyes.

3.2.1 Cationic Dyes

Table 3.1: List of available cationic dyes in the laboratory

	Sandocryl Cationic dyes	**Code**	**Solubility**
1	Marine Blue	B-RL	Tested
2	Blue	B-RLE	Tested
3	Red	B-RLN	Tested
4	Schwarz	B-RL Conc.	Tested
5	Golden Yellow	B-GRL	Tested
6	Brilliant Yellow	B-6GL	Tested
7	Schwarz	C-MP	Tested
8	Red	C-RLP	Tested
9	Golden Yellow	C-GL	Tested
10	Blue	C-RLP	Tested
11	Schwarz	S-BLN	Tested
	Astrazon Basic Dyes		
12	Golden Yellow	GL-E	Tested
13	Red	FBL	Tested
14	Red	GTLN	Tested
15	Blue	FGGL	Tested
16	Green	M	Tested

Test Procedures 1

A small amount of dyestuff from all 16 available dyes was placed inside a test tubes followed by small addition of the Isopropyl alcohol solvent which was estimated to be about 5ml. The dye solution in each test tube was shaken and given 30 minutes for the dye to dissolve than the results were evaluated by means of the visual method using the following questions:

- Observations of the dissociation of the dye particles in the solution by observing the bottom of the test tube of the presence of dye particles.
- Looking and selection of dyes according to their shade and depth without regards to dye concentration values being known.

Test Procedures 2

The purpose of this step was to create small samples of selected 6 dyes which were to undergo further test by means of spectroscopy.
This test has to be carried out wit the greatest care in order to obtain accurate results.

100 ml of Isopropyl alcohol solvent
0.1g/l of dyestuff

Calculations:
0.1g 1000ml
Xg 100ml

X=0.01g of dyestuff

0.01g of dyestuff for all 6 available dyes were weighed and placed inside 6 small bickers and addition of 100ml of solvent inside each bickers by using the pipette.

Figure 3.2: *Scales used for weighing of dyes*

A
These samples are further tested by means of extracting 2 ml of the dye solution from each bicker and placing the 2ml of solution in the clean tested tube and followed by adding 48 ml of the isopropyl alcohol solvent in the solution this were also shaken and given 20 minutes for the dyes to dissolve. Afterwards these samples were taken to another laboratory for spectroscopy testing whereby graphs and values were obtained for concentration and absorbency curves.

B

The remaining 48 ml of dyes solution from the first preparation is used for colouring strips of Glass filter paper. These dye solution was also used for making spot test sample by using the pipette to place dye solution drops on the surface of the glass fibre and dry firstly at room temperature followed by hot air fixation at 90^0C for 3 hours.

The strips were prepared by holding the other end of the strip and deep it in the test tube with the dye solution for 1-2 seconds followed by dry at room temperature for + 30 minutes. After drying at room temperature, they are fixed for 3 hours at 90^0C.

Test Procedure 3

After obtaining the results from the previous tests, the selected dyes 6 dyes were further test by making a dye solution using the special solvent, which will be used for the colouration stage for our selected fabrics, the following recipe was prepared:

0.1g of dye concentration
50 ml of the TMSPM solvent
Calculations:

0.1g	1000ml
Xg	50 ml

X=0.005g of dyestuff

Glass filter paper samples were obtained and were dyed using the calculated dye solution. This is done with the aim of visual assessing if the dye stuff will be able to colour the glass paper, and the depth of colour will be majored to observe if dark shades can be achieved by using these dyestuffs on selected fabrics.

Samples were padded on a tray with dye solution at room temperature, taken to the mangle machine to ensure levelness of dyes through the sample. These were dried in the laboratory at room temperature followed by dye fixation using hot air at 90^0C for 3 hours. The results were obtained for visual evaluations.

3.2.2 Disperse and Metal Complex Dyes

The experiments conducted for these two classes of dye stuff are similar and these experiments were performed simultaneously.

Table 3.2: List of Disperse and Metal Complex dyes available in the lab:

	Disperse dyes /Ostracet dyes	**Code**	**Solubility**
1	Foron Brilliant Red	S-GL	Tested
2	Brilliant Red	E-LB	Tested
3	Red	S-B	Tested
4	Red	E-L2B	Tested
5	Violet	E-G	Tested
6	Orange	SE-2G	Tested
7	Gold	E-LR	Tested
8	Gold	SE-LG	Tested
9	Gold	B-L5R	Tested
10	Blue	E-LG	Tested
11	Blue	S-LB	Tested
12	Light Blue	S-G	Tested

	Metal Complex Dyes /Chromolan dyes	**Code**	**Solubility**
1	Red	GRE	Tested
2	Olive	5R	Tested
3	Marron	RM	Tested
4	Gold	GR	Tested
5	Gold	R	Tested
6	Brown	R	Tested
7	Brown	G	Tested
8	Blue	GG (15B)	Tested
9	Blue	GG	Tested
10	Green	BL	Tested
11	Black	WAX	Tested

Test Procedure 1

The same test procedure conducted for Cationic dyes was also performed for these two classes of dyes stuffs. Except that small samples were obtained by the method of spot tests using the glass filter paper and the dyes were selected according to the results of the spot test.

Test Procedure 2

The dyes which are selected by using the above method were further tested for solubility by weighing the small amount of dyestuff; about 0.1g and placing it in the graduated cylinders followed by adding of 10 ml of isopropyl alcohol solvent at 5 minutes time intervals up until maximum solubility of dyes in the solution is achieved. After obtaining the correct volume of the solvent at which the dyes are soluble at, calculations were made.

3.2.3 Selected dyes for further testing

Procedure 1

Figure 3.3: *The centrifugal machine for segmentation of dye particles in a solution*

For this test all selected dyes from all three classes including Cationic dyes were tested at once. A larger amount of dyestuff for each selected dyes is added to 14 test tubes and about 10 ml of our selected solvent AC+BPO+0.3 is also added to create a dye solution, these dye solutions are shaken and given 30 minutes for dissociation in the solution and for the undissolved dye particles to settle to the bottom of the test tube. The dye solution is then transported to the centrifugal machine which runs at 40 rpm for 2 minutes, after this process maximum solubility of dyes is achieved and segmentation of dye particles occurs.
Three strips of glass filter paper are dyed for each dye which is being tested, 5x5 cm samples of the same fabric also dyed, two of each dye samples. The spot test is also prepared for all available dyes for testing. This were dyed using the following parameters:

Spot test

About 0.5 ml of dye droplets are placed of the surface of the glass filter paper and dried at room temperature for 30-40 minutes, followed by fixation at 90^0C for 3 hours.

Glass Strips

These were inserted in the solution for 1-2 seconds followed by drying at room temperature for 30-40 minutes. After drying these are fixed in the drier at 90^0C for 3 hours

5x5 glass filter samples
These were placed on a raised flat steel net followed by padding with the dyes solution of 0.5 ml x 3=1.5 ml, the pipette used was F500. This are left there on the steel net to dry for 30-40

minutes at room temperature, followed by fixation in the drier with hot air at 90^0C for 3 hours. Further test will be done on these samples to observe the behaviour of our selected dyes and best dyes will be selected for further work.

Procedure 2

After samples were fixed for 3 hours, these had to be tested for dye properties, 2 sets of 5x5 samples were cut to 8 equal pieces, one sample being a standard and the rest are used for testing of following fastnesses:

1. Wash Fastness

One sample is used for testing wash fastness, the sample is placed inside the test tube and 10 ml of water is added followed by heating at the stove at 60^0C for 60 minutes. The samples are removed the resulted solution is tested in a spectroscopy for how much dye has been removed from the dyed Glass filter paper by hot water.

2. Temperature Fastness

Four samples were used at different temperature for testing of dye fastness to high temperatures. The heating box which can reach high temperature parameters is used for conducting this experiment. Samples were tested at selected temperature for 5 minutes each. The following temperature parameters were used:

Figure 3.4: *Heating box for high temperatures*

200^0C for 5 minutes
300^0C for 5 minutes
400^0C for 5 minutes
500^0C for 5 minutes

Caution must be applied carefully when using the heating box because if temperatures above the degradation temperature of the fabric is used the material will be burned, also heating time must be controlled.

3. Light Fastness

Two samples are used for testing of fastness to light using the using the UV light at a distance of 23.5 cm. The first samples are exposed to UV light for 20 minutes and the second samples are exposed for 120 minutes, the results are evaluated using the blue scale.

4. Evaluation of fixation time at 90^0C

6 samples from 14 selected dyes were prepared using the same recipe as the one used for preparing the fastness samples. These samples were fixed at different times from 1-6 and afterwards the results were evaluated using the wash fastness method, where the dye absorbency was measured using the spectrometer with the wavelengths values being obtained from the previous wash fastness test in number 1.

The samples were also further tested using a spectrometer for colour measurements, so that the differences in Lightness of colours and colour difference at different fixation times can be plotted on the graph.

4. RESULTS AND DISCUSSIONS

In this chapter results of all the experiments conducted for this study will be posted here and be explained and discussed. The data collected from the experiments may come in different form such as drawings, pictures, graphs, calculations etc. All of the work done in the laboratory in regards to this study is discussed here including successes and failures. A reader may take note that the numbering and headings in this chapter matches the numbering and headings in the previous ***Chapter 3*** so that one reading may clear follow and refer to the experimental data with ease.

3.2.1 Cationic Dyes (Results)

Procedure 1

This experiment was conducted according to the mentioned procedure in ***chapter 3*** under the heading ***Cationic Dyestuffs*** and the following results were obtained.

Table 4.1: List of selected cationic dyes

	Sandocryl Cationic dyes	**Code**	**C.I. name**	**C.I number**	**Solubility**
1	Golden Yellow	C-GL	C.I Basic yellow	28	Soluble
2	Blue	C-RLP	C.I Basic Blue	Not availabl	Soluble
	Astrazon Basic Dyes				
3	Golden Yellow	GL-E	C.I Basic Yellow	28	Soluble
4	Red	FBL	C.I Basic Red	46	Soluble
5	Red	GTLN	C.I Basic Red	18	Soluble
6	Blue	FGGL	C.I Basic Blue	41	Soluble

Discussion 1

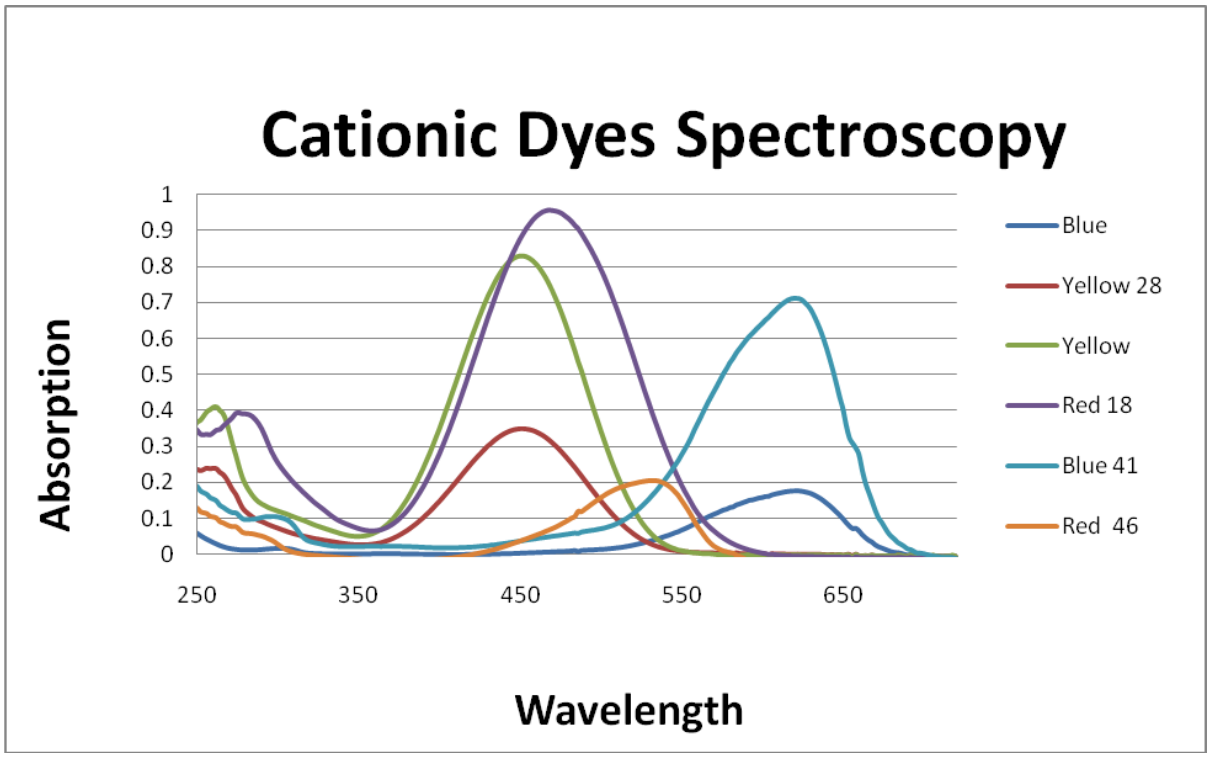
The evaluation method for the above results, was simply visual observation between two people who were involved in conducting this experiment, the results are obtained from the following two criteria:

- Observations of the dissociation of the dye particles in the solution by observing the bottom of the test tube of any presence of dye particles.
- Looking and selection of dyes according to their shade and depth without regards to dye concentration values being known.

The above listed dyes seemed to comply with the set standards for visual evaluation of dyes, whilst other dyes which were also selected for this showed signs of poor solubility to the isopropyl alcohol solvent.

Procedure 2A

The dyes which were selected in ***procedure 1*** were selected to undergo spectroscopy testing and the following curves on the graph were obtained.



	Yellow 28	Yellow 28.	Red 18	Red 46	Blue-	Blue 41
Wavelength	450	450	468	532	622	620
absorption	0.34	0.82	0.95	0.20	0.17	0.71

Figure 4.1: *Spectroscopy results for cationic dyes*

Discusion 2A

The curves of the selected dyes in the above graph are siutable for the proposed work which is selecting of dyes for colouration of three kinds of special fibers aramide, polypropylene and glass fibers. They all fall within the visible regions respectably, between 400nm and 750nm at small concetration of dyes in the isopropyl alcohol solvant. Below the graph there is a small table which explains clear, what results for each selected dyestuff were obtained under the spectroscopy measuring instrument.

Procedure 2

This result are obtained from the second remaing dye solution of 48 ml, whereby small drops of dye are pippetted on the surface of the glass filter paper. There is also the dyeings of small

strips of glass filter paper which is deeped in the dye solution for 1-2 seconds followed by the drying at room temperature and then treated by hot-air at 90^0C for 3 hours.

Table 4.2: List of basic dyes used for the spot ***(figure 4.2)*** and Stripes ***(figure 4.3)*** tests

	C.I. name	**C.I number**	**Solubility**
1	C.I Basic yellow	28	Soluble
2	C.I Basic Yellow	28.	Soluble
3	C.I Basic Red	46	Soluble
4	C.I Basic Red	18	Soluble
5	C.I Basic Blue	-	Soluble
6	C.I Basic Blue	41	Soluble

Figure 4.2: *Spots test for visual evaluation of cationic dyes*

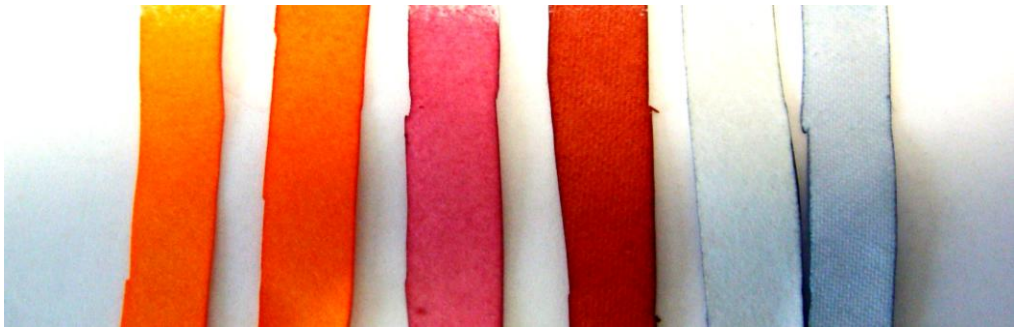


Figure 4.3: *Stripes of dyed glass filter paper using cationic dyes for visual purposes*

Discussion 2B

By looking at both figures above ***Figure 4.2 & 4.3,*** it is visually clear that the yellow and the red dyestuff have deeper shades and there seemed to be level without the use of a padded, whilst the blues at same concentrations resulted to lighter shades. This may be the result of low solubility to the solvent or low dye affinity for the fibre. Although tests such as wet, light and heat (temperature) fastnesses were not performed for these particular experiments, the purpose of these experiments were to observe if the selected cationic dyes based on the visual selection test performed in ***Procedure 1*** would be able to colour the surface of the glass filter

paper and be able to stay bonded with the filter paper after fixation with hot air at 90^0C for 3 hours or the dyes would evaporate in air during the fixation stage. As a result the dyes proved to stay bonded even after hot-air fixation; the resultant colours especially the yellows and reds are satisfying.

Procedure 3

The results for this experiment are placed below followed by their discussions. the here was to observe how would a dye react with the selected solvent which was going to be used for the final laboratory dyeing of selected fibres for this study.

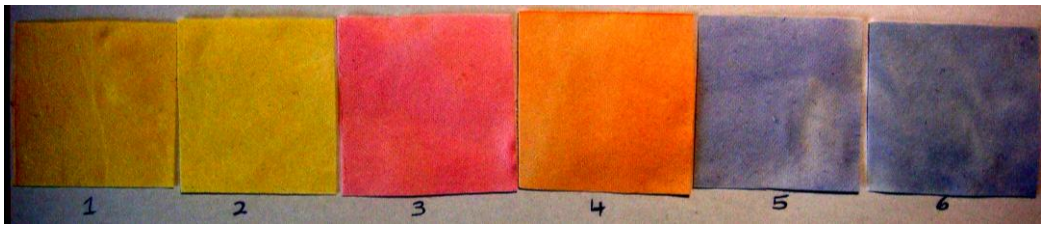


Figure 4.4: *Cationic Dyes and TMSPM (DO-Sol GEL) solvent samples*

Discussion 3

The shades obtained in these samples are much lighter but that may be due to the fact that a small concentration of dye was used and mostly the some of the dye stuff was squeezed out of the filter paper when passed through a mangle. The samples have a dark and light place which means that the dye is not level throughout the whole sample; the reason for padding with the mangle was to ensure levelness of dye through out the sample. These samples were only suitable for visual observations none of the fastness tests were done on these samples. There was however some unsuitable drawbacks about the padding method the handle of the samples was not affected but the samples were easily damaged by touching which clearly states that somehow there was a decrease in fibre cohesion within the fabric strength.

3.2.2 Disperse and Metal Complex Dyes (Results)

Procedure 1

The following results (figures) and the table is the list of dyes which were selected in both Disperse Dye and Metal Complex dye classes. The procedure for these experiments was
Similar to the one conducted for Cationic dyes as described in the previous ***Chapter 3,***

1 2* 3 4 5 6 7 8* 9* 10* 11 12

Figure 4.5: *Spot test results for Disperse dyes which were tested for solubility in lab*

1* 2 3 4* 5 6 7 8* 9 10 11*

Figure 4.6: *Spot test results for Metal Complex dyes which were tested for solubility in the lab, the ones with the star on top were selected for further testing*

Discussion 1

After making of the dye solutions from both dye classes disperse and metal complex dyes a spot test was done for all of the involved dyes and dyes with a star on top of the number were selected based on how the shades looked visually refer to ***Table 4.3*** below, in case of the Metal complex dyes there were big signs of dyes not having a high degree of solubility in isopropyl alcohol solvent this can be easily observed in ***Figure 4.6*** where the dye stuff seems to have two spheres the centre being darker than the outer sphere; a method for increasing the solubility of dye is to be employed for the following experiments.

Table 4.3: List of selected Disperse and Metal complex dyes

	Ostracet Disperse Dyes	**Code**	**C.I. name**	**C.I number**	**Solubility**
2	Brilliant Red	E-LB	C.I Disperse Red	60	Soluble
8	Gold	SE-LG	C.I Disperse yellow	42	Soluble
9	Gold	B-L5R	C.I Disperse yellow	23	Soluble
10	Blue	E-LG	C.I Disperse Blue	81	Soluble
	Metal Complex Dyes				
3	Maroon	RM	C.I Acid red	179	Soluble
4	Gold	GR	C.I Acid yellow	99	Soluble
8	Blue	GG	C.I Acid Blue	158	Soluble
11	Black	WAX	C.I Acid Black	52	Soluble

Procedure 2

Further experiments for testing of solubility for the selected dyes in ***Table 4.3*** were conducted. These experiments involved that, 0.1g of dyestuff was inserted into a graduated glass cylinder followed by additions of 10ml of isopropyl alcohol solvent at 5 minutes intervals up until the dye reaches its maximum solubility in the solution.

Discussions 2

After the solubility of dyes was reached calculations were done to observe in how many ml of solvent is 0.1g of dye is 100% soluble? The following are the results obtained from these experiments:

Disperse Dyes

Red E-LG
40 ml of solvent was used for dilution
0.01 g of dye

0.01g 40 ml
X 1000ml
X = 0.25g of dye

Gold SE-LG
40 ml of solvent was used for dilution
0.01 g of dye

0.01g 40 ml
X 1000ml
X = 0.25g of dye

Gold B-L5R
160 ml of solvent was used for dilution
0.01g of dye

0.01g 160 ml
X 1000ml
X = 0.06g of dye

Blue E-LG
90 ml of solvent was used for dilution
0.01g of dye

0.01g 90 ml
X 1000ml
X = 0.11g of dye

Metal complex Dyes

Maroon RM
110 ml of solvent was used for dilution
0.1g of dye

0.1g 90 ml
X 1000ml
X = 0.9 g of dye

Gold GR
500 ml of solvent was used for dilution
0.1g of dye

0.1g 500 ml
X 1000ml
X = 0.2g of dye

Blue GS
450 ml of solvent was used for dilution
0.1g of dye

0.1g 450 ml
X 1000ml
X = 0.22g of dye

Black WAX
380 ml of solvent was used for dilution
0.01g of dye

0.1g 380 ml
X 1000ml
X = 0.26g of dye

3.2.3 Selected dyes for further testing (Results)

Procedure

In this experiment all 14 selected dyes from the three previously mentioned classes are all tested together and their evaluation was based on 3 fastnesses tests; wash, temperature and light.

Table 4.4: The list of all 14 selected Dyes for fastness test properties

	Selected Dyes	**Code**	**C.I. name**	**C.I number**	**Solubility**
1	Maroon	RM	C.I Acid red	179	Soluble
2	Gold	GR	C.I Acid yellow	99	Soluble
3	Blue	GG	C.I Acid Blue	158	Soluble
4	Black	WAX	C.I Acid Black	52	Soluble
5	Brilliant Red	E-LB	C.I Disperse Red	60	Soluble
6	Gold	C-RLP	C.I Disperse yellow	42	Soluble
7	Gold	B-L5R	C.I Disperse yellow	23	Soluble
9	Blue	E-LG	C.I Disperse Blue	81	Soluble
10	Golden Yellow	C-GL	C.I Basic yellow	28	Soluble
11	Golden Yellow	GL-E	C.I Basic Yellow	28.	Soluble
13	Red	FBL	C.I Basic Red	46	Soluble
13	Red	GTLN	C.I Basic Red	18	Soluble
14	Blue	FGGL	C.I Basic Blue	41	Soluble
15	Blue	C-RLP	C.I Basic Blue	-	Soluble

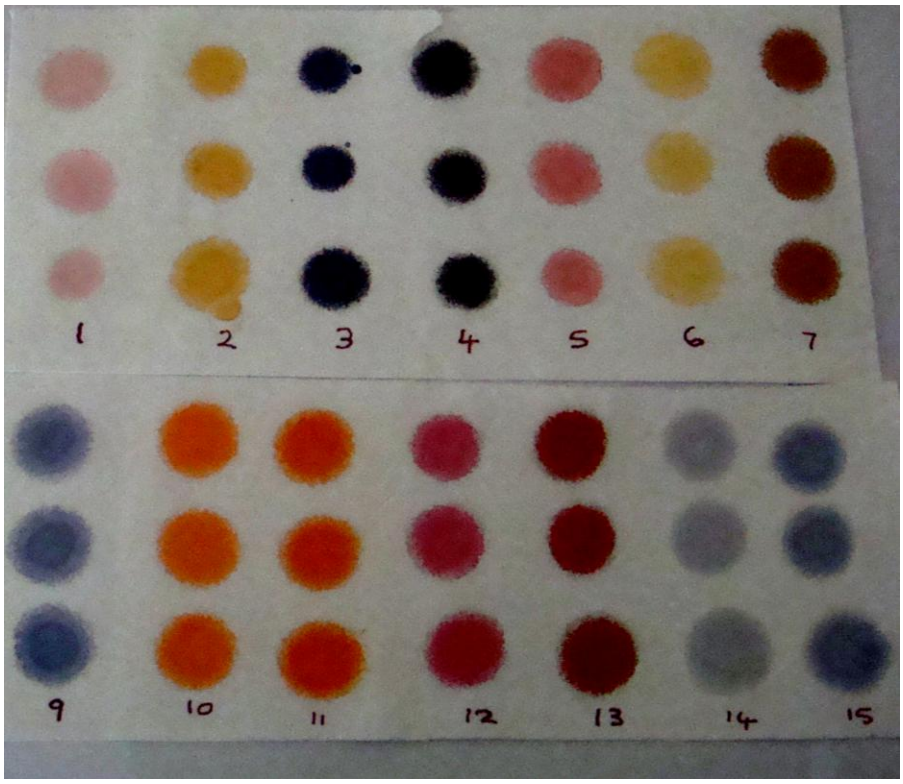


Figure 4.7: *Spots test for visual evaluation of shades for the selected dyes using the TMSPM solvent*

1 2 3 4 5 6 7 9 10 11 12 13 14 15

Figure 4.8: *Strips of samples obtained for visual observations*

After samples were fixed for 3 hours, these had to be tested for dye properties, 2 sets of 5x5 samples were cut to 8 equal pieces, one sample being a standard and the rest are used for testing of following fastnesses:

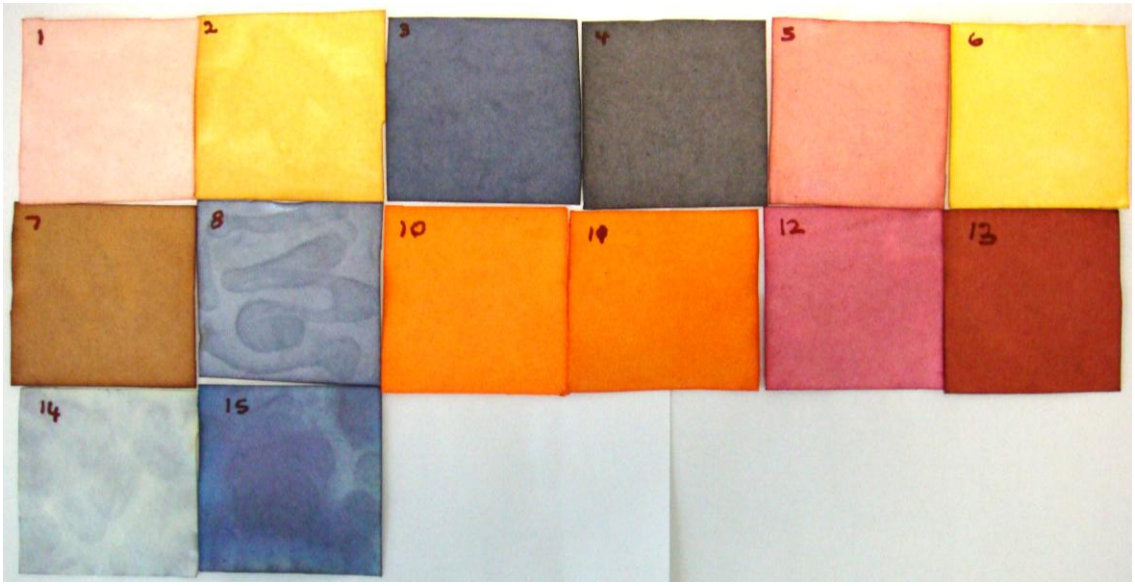


Figure 4.9*: 5x5 samples for testing of dye properties*

<u>Discussions 1</u>

By visually evaluations of sample especially in the above figure 4.8 it is visually clear that, there are some problems with the solubility of some of the dyes especially the blues numbers 8, 14 and 15 they are clearly showing big unlevelness of dye throughout t the glass filter paper, this

may be due to poor solubility of dyes in the solvent or it may be caused by a wrong technique of padding the dyes on the surface of the glass filter paper. This problem will be looked at deeply as the experiments progresses to the next levels. These samples are tested for fastness properties in the next stage of experimenting.

Procedure 2

The above samples in ***Figure 4.5*** were all tested for dye properties to the fibre (glass filter paper) and the following results were obtained.

1.Wash fastness

One sample from each dyestuff is testes for the wash fastness properties by using water at 60^0C for 1 hour. The following spectroscopy results were obtained.

Table 4.5: all dyestuffs which have been tested for wash fastness properties using the spectroscopy as the evaluating to*ol.*

M. Complex	Acid red 179	Acid Yell 99	Acid Blue 158	Acid Black 52
Wavelength	504	450	624	570
absorbency	0.1	0.5	2.2	1.2

Disperse Dyes	Disperse Red 60	Disp Yellow 42	Disperse Yellow 23	Disperse Blue 81
Wavelength	400	406	400	582
absorbency	0,01	0.1	0.1	0.1

Cationic Dyes	Yellow 28	Yellow 28.	Red 46	Red 18	Blue 41	Blue -
Wavelength	402	396	524	486	486	600
absorbency	4	4	0.6	3.5	0.1	0.2

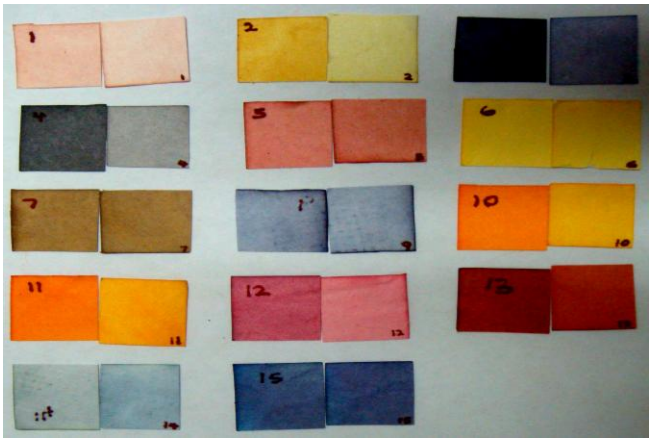


Figure 4.10: *above are the wash fastness results*

Discussion

By looking at the spectroscopy result in the above tables in ***Figure 4.5***, it is visible clear that the disperse dyes have a higher fastness properties compared with the Metal complex in second place and Cationic Dyes in third place. This can be observed by looking at the lower absorbency values of the disperse dyes compared with those of the other dyes. This can also be observed by looking at the differences between the original samples and the wash fastness samples in ***Figure 4.6***.

2. Temperature fastness

Four samples were used for evaluation of stability at different temperatures for testing of dye fastness to high temperatures. 4 set of sample from the selected 14 dyes were tested at different temperatures for 5 minute each set. The results were evaluated by colour measurement spectrometer and visual observation in comparison to the original untreated sample. Unfortunately due to time constrains only the 200^0C graphs are plotted in these report the rest will be available for presentation.

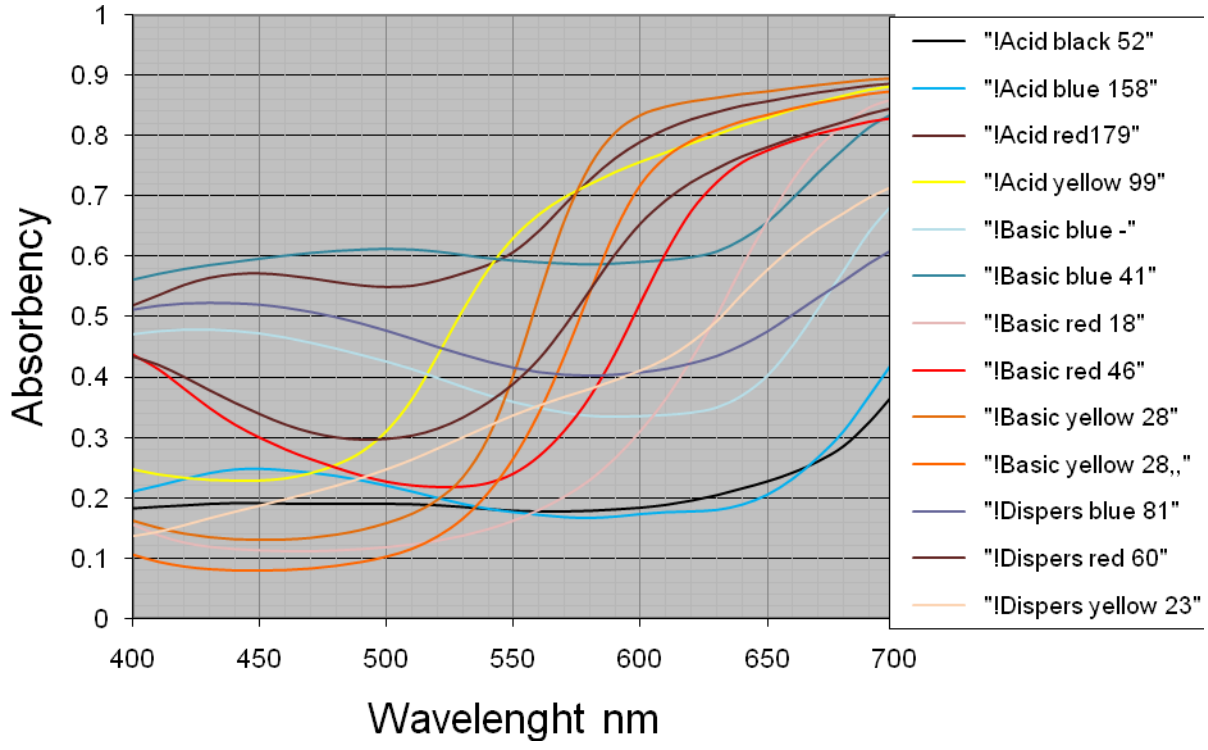
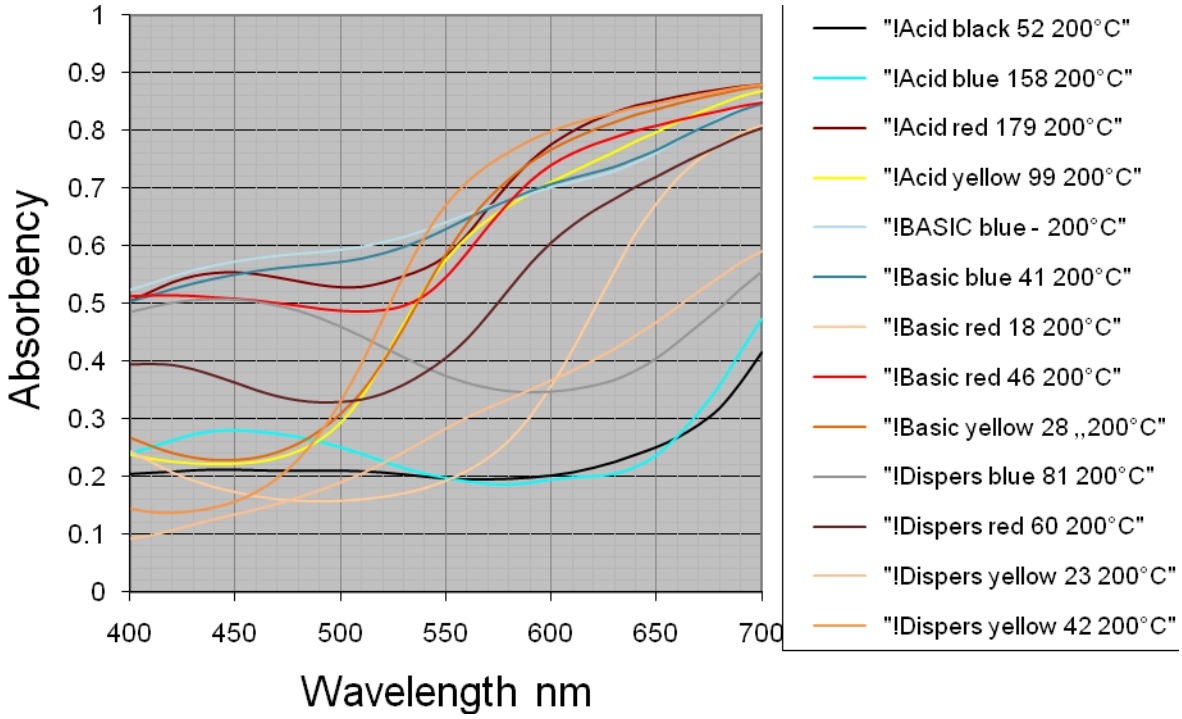


Figure 4.11: *Graph curves for standard samples for comparison with tested samples*



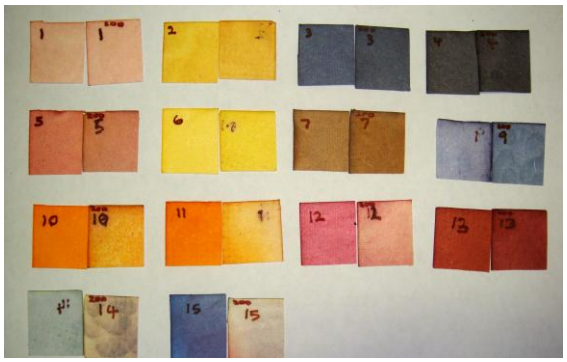


Figure 4.12: *above are the results for high temperature stability at 200^{0}C*

Discussion

The Metal Complex and the Disperse dyes in ***Figure 4.11,*** by looking at the first photo with 200^{0}C temperature, these dyes are a bit stable at this temperature but we must keep in mind that there were only exposed for 5 minutes, whilst the Cationic dyes are already showing signs of the colour fading in this photo. The graphs above can explain the changes which occurred during high temperature exposure at 200^{0}C. This can be observed by looking at the absorbency or dye concentrations present before (***Figure 4.10)*** and after the material have been heated at high temps. For further analysis please look at the photos in the last appendix page

3. Light fastness

Two samples are used for testing of fastness to light using the using the UV light at a distance of 23.5 cm. The first samples are exposed to UV light for 20 minutes and the second samples are exposed for 120 minutes, the results are evaluated using the blue scale. The following results were obtained.

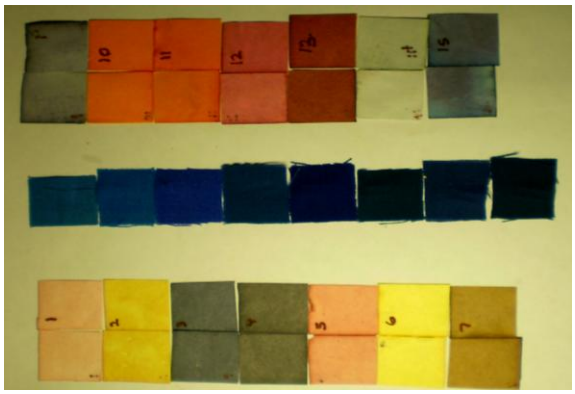


Figure 4.13: *first samples exposed to UV light for 20 minutes*

Table 4.6: light fastness results of first samples from the blue scale in ***Figure 4.12*** above

Sample No	Results	Sample No	Results
1	1	9	2
2	2	10	3
3	3	11	3
4	3	12	3
5	3	13	4
6	3	14	1
7	4	15	2

Figure 4.14: *second set samples exposed to UV light for 120 minutes*

Table 4.7: fastness results of second samples from the blue scale in ***Figure 4.13*** above at 120 minutes

Sample No	Results	Sample No	Results
1	1	9	1
2	3	10	3
3	2	11	2
4	2	12	2
5	2	13	3
6	2	14	1
7	3	15	1

Discussion

The results above are obtained using the blue scale in the middle of both photographs, in the first samples in ***figure 4.12***, there is not too much effect caused by the UV light to the samples and that can be seen by looking at the original samples the ones on the inside with the visible sample numbers and the one without the sample numbers are the ones which have been exposed to the UV light. The light fastness of the dyes decreases as the exposure to the UV light increases from 20 minutes to 120 minutes.

4. Evaluation of fixation times at 90^0C

6 samples from 14 selected dyes were prepared using the same recipe as the one used for preparing the fastness samples. These samples were fixed at different temperatures from 1-6 and afterwards the results were evaluated using the wash fastness method, and the following results were obtained:

Tables 4.8: results obtained from the spectroscopy for evaluation of the wash fastness using different fixation temperatures

M. Complex	Fixation	Red 179	Yellow 99	Blue 158	Black 52
Wavelength	Hours	504	450	624	570
absorbency	1	0. 141	0.650	1.627	0.646
	2	0.097	0.697	1.553	0.541
	3	0.213	0.460	1.727	0.690
	4	0.330	0.427	1.826	0.675
	5	0.135	0.605	1.634	0.518
	6	0.108	0.545	1.466	0.413

Disperse Dyes	Fixation	Red 60	Yellow 42	Yellow 23	Blue 81
Wavelength	Hours	400	406	400	582
absorbency	1	0.038	0.089	0.136	0.026
	2	0.036	0.138	0.110	0.028
	3	0.029	0.124	0.081	0.069
	4	0.032	0.098	0.076	0.024
	5	0.033	0.104	0.066	0.027
	6	0.58	0.094	0.099	0.022

Cationic Dyes	Fixation	Yellow 28	Yellow 28	Red 46	Red 18	Blue 41	Blue -
Wavelength	Hours	402	396	524	486	486	600
absorbency	1	3.555	3.503	0.744	1.904	0.046	0.008
	2	3.555	3.503	0.789	1.611	0.040	0.039
	3	3.497	3.503	0.725	1.530	0.036	0.091
	4	3.497	3.561	0.398	1.365	0.029	0.081
	5	3.497	3.561	0.496	1.564	0.050	0.038
	6	3.497	3.561	0.344	2.932	0.056	0.009

Discussion

The results above states that it is much better to use different fixation temperatures for each dyes in all selected dye classes, although generally the most possible fixation temperature for these dyes is about 3 hours at 90^0C. When analysing the results above it is visible clearer that the Disperse dyes have a higher wash fastness property compared with the Metal Complex and Cationic dyes which have much lower wash fastness property except for the blue colours, the yellows are not suitable for good fastness requirements.

Procedure 2

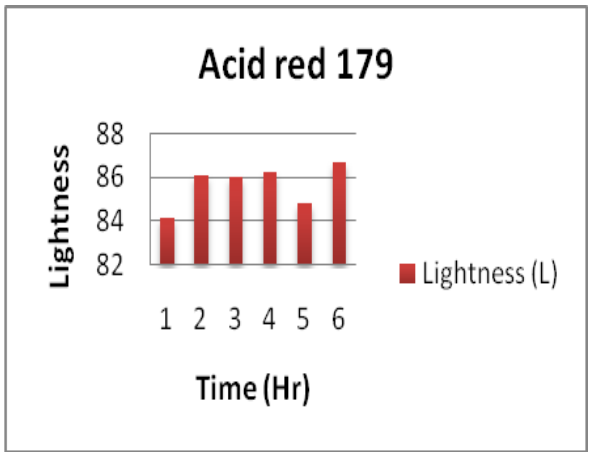
The samples were also tested for colour differences and lightness using the spectrometer colour measurement device. The standard samples were obtained from ***(Figure 4.8)*** these are compared with the other 6 samples, at different temperatures to obtain the colour difference values.

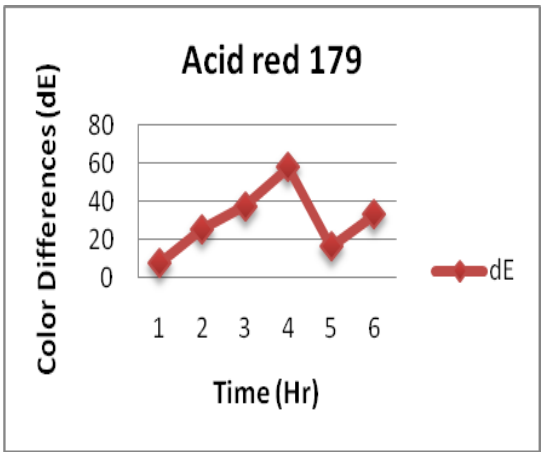
Table 4.4: The list of all 14 selected Dyes for fastness test properties

	Selected Dyes	**Code**	**C.I. name**	**C.I number**	**Solubility**
1	Maroon	RM	C.I Acid red	179	Soluble
2	Gold	GR	C.I Acid yellow	99	Soluble
3	Blue	GG	C.I Acid Blue	158	Soluble
4	Black	WAX	C.I Acid Black	52	Soluble
5	Brilliant Red	E-LB	C.I Disperse Red	60	Soluble

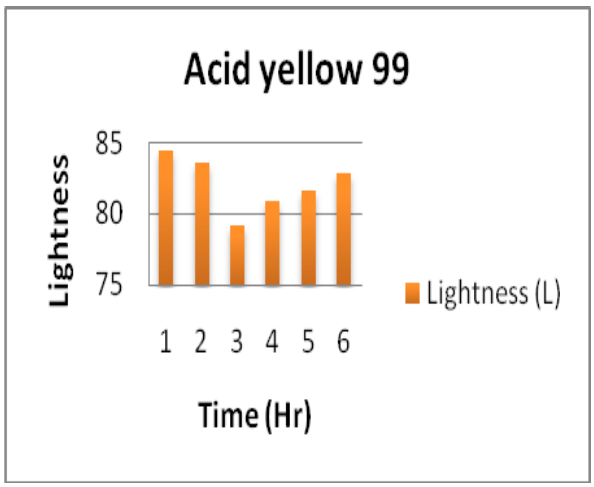
6	Gold	C-RLP	C.I Disperse yellow	42	Soluble
7	Gold	B-L5R	C.I Disperse yellow	23	Soluble
8	Blue	E-LG	C.I Disperse Blue	81	Soluble
9	Golden Yellow	C-GL	C.I Basic yellow	28	Soluble
10	Golden Yellow	GL-E	C.I Basic Yellow	28.	Soluble
11	Red	FBL	C.I Basic Red	46	Soluble
12	Red	GTLN	C.I Basic Red	18	Soluble
13	Blue	FGGL	C.I Basic Blue	41	Soluble
14	Blue	C-RLP	C.I Basic Blue	-	Soluble

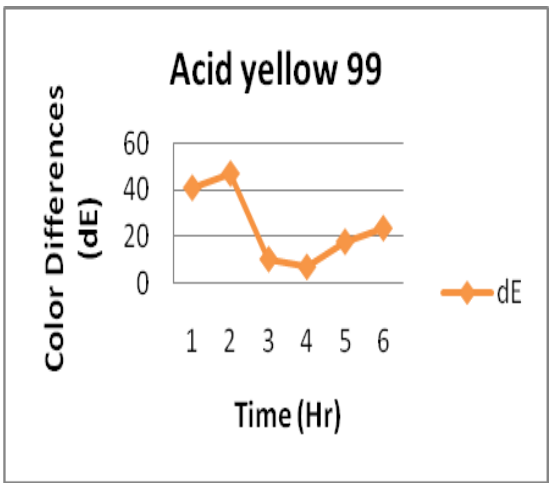
1. C.I Acid red 179



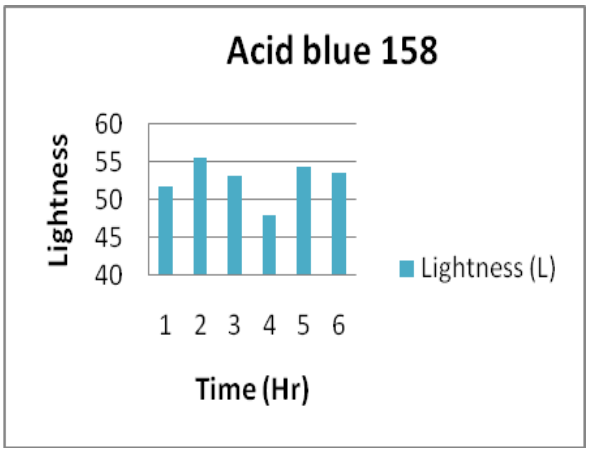


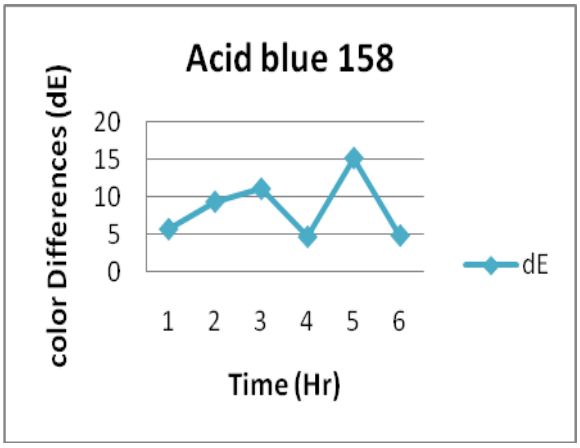
2. C.I Acid yellow 99



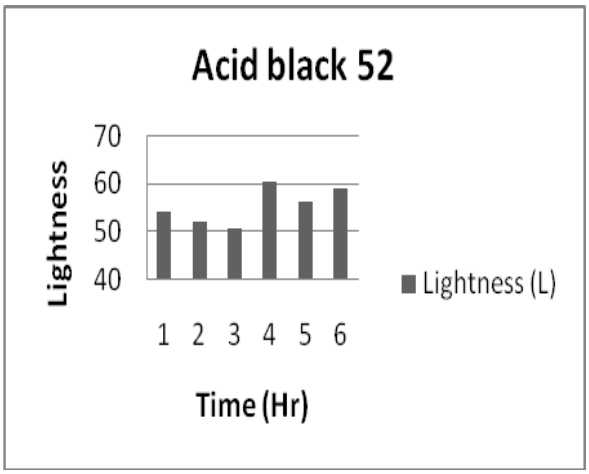


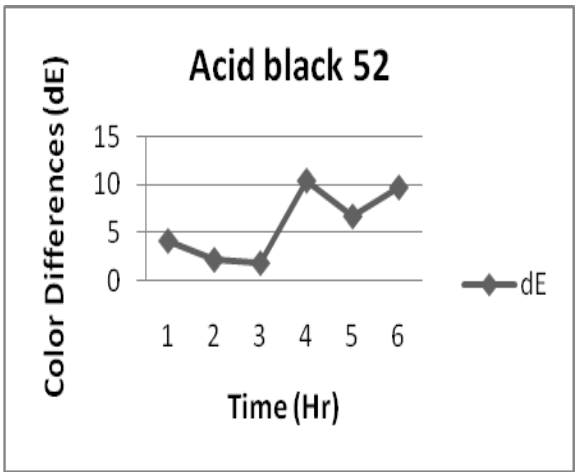
3. C.I Acid Blue 158



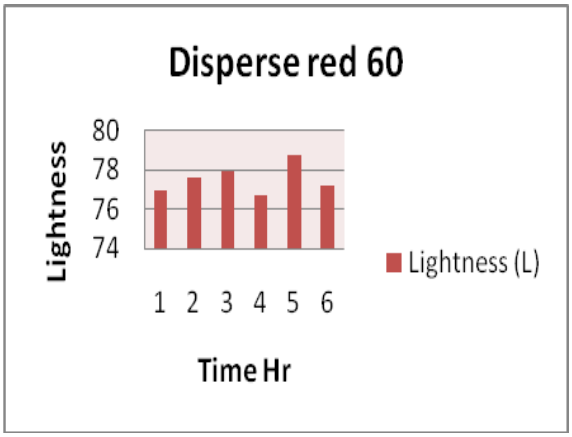


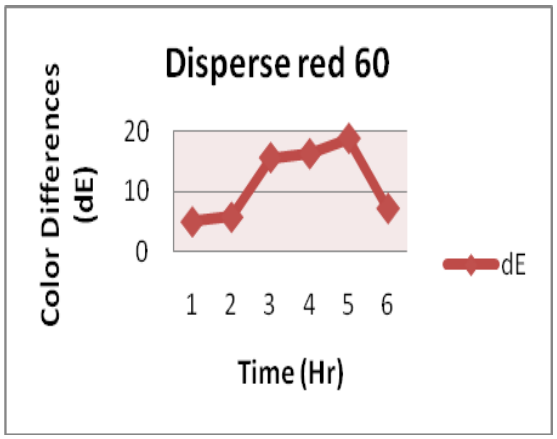
4. C.I Acid Black 52



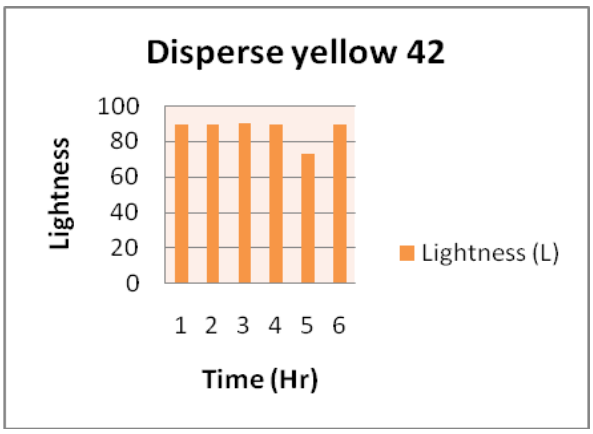


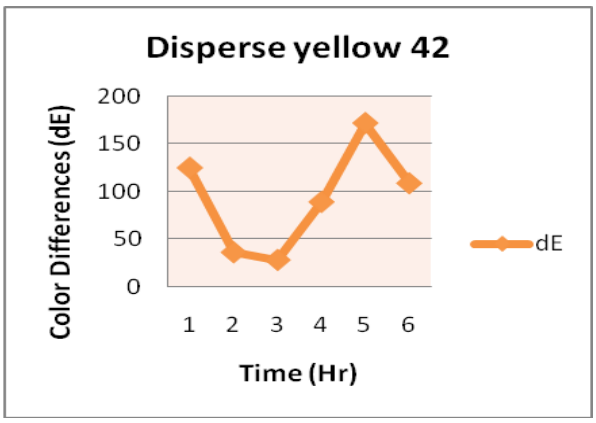
5. C.I Disperse red 60



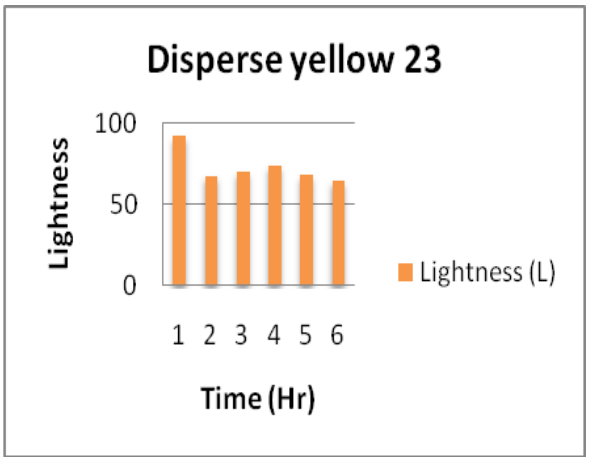


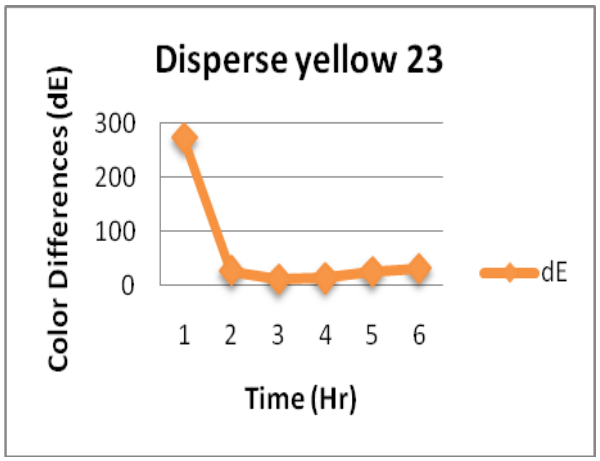
6 C.I. Disperse yellow 42



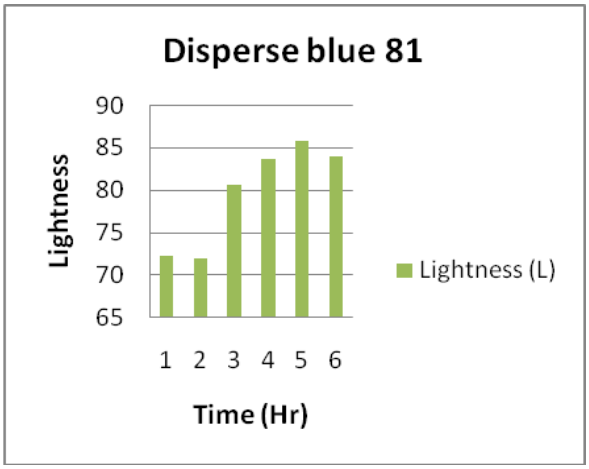


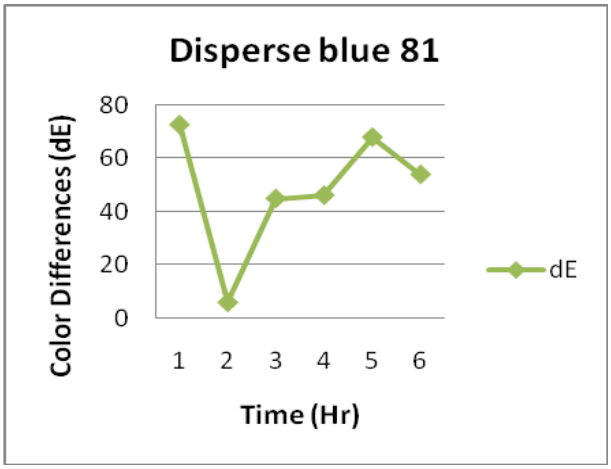
7. Disperse yellow 23





8. C.I. Disperse blue 8





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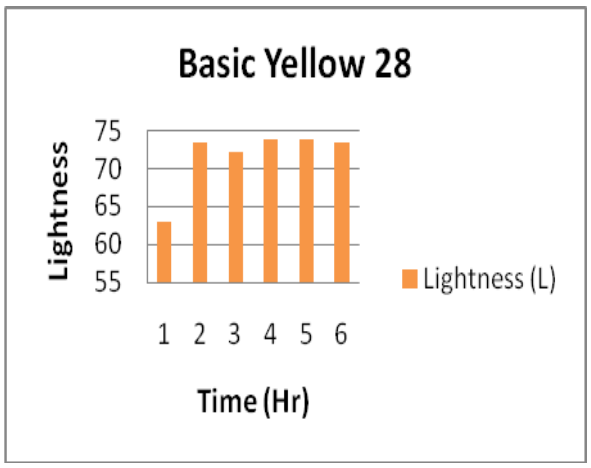

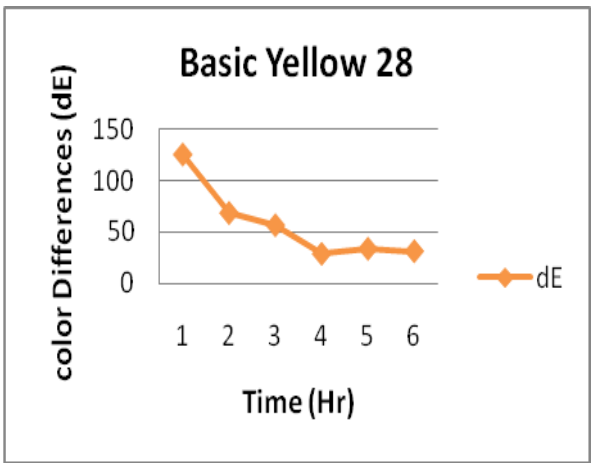

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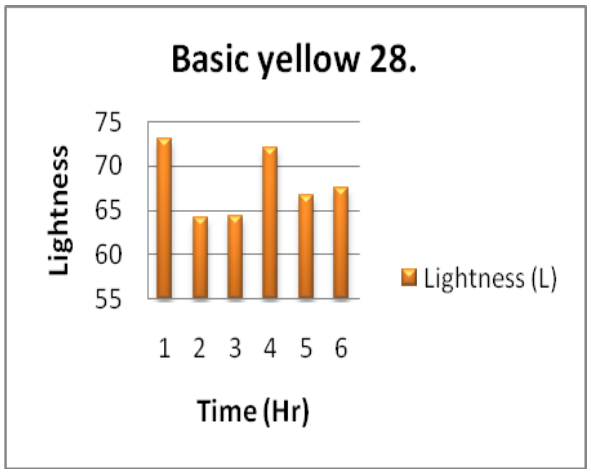

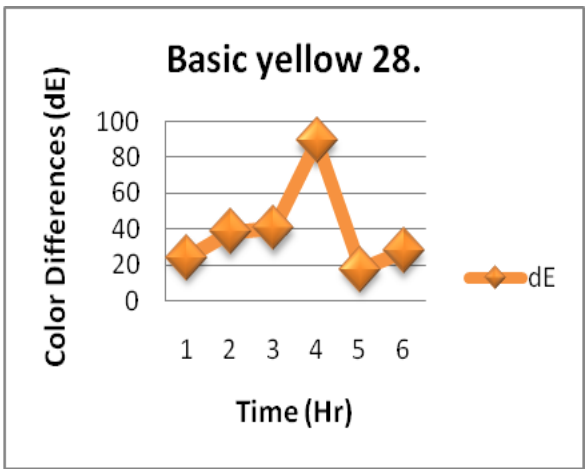

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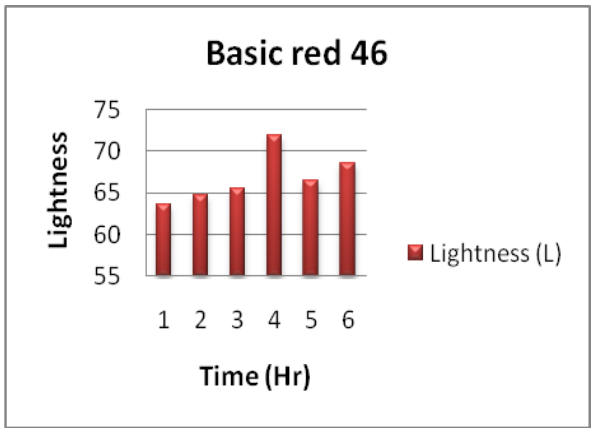

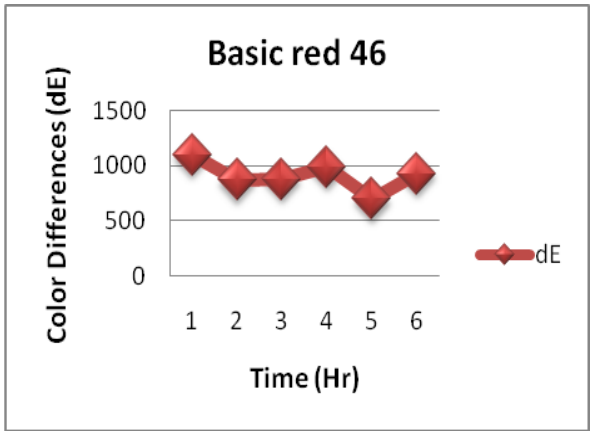

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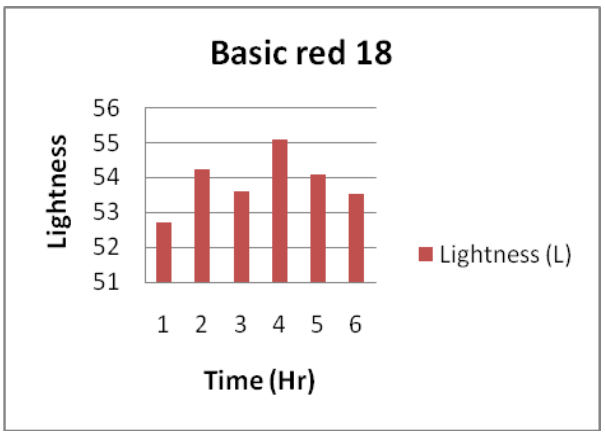
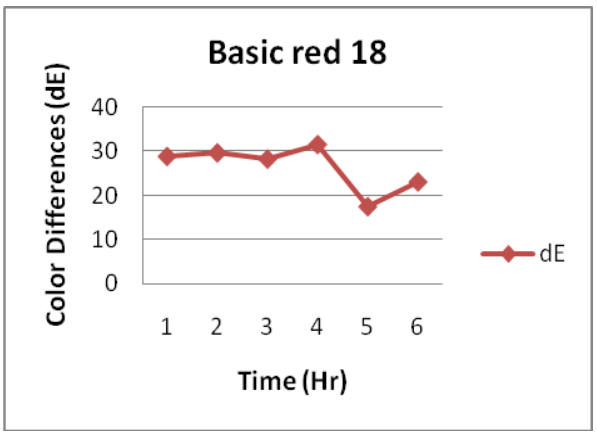
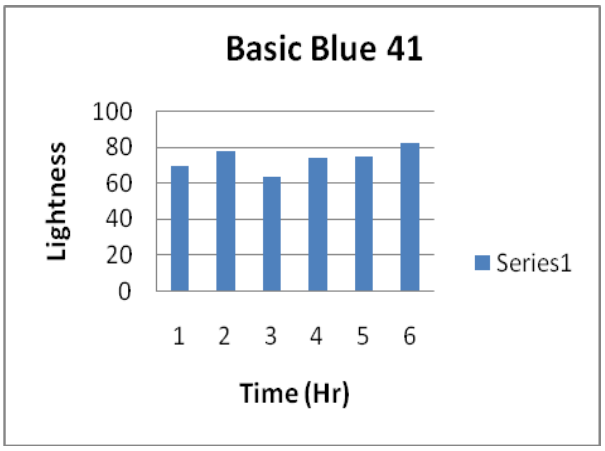
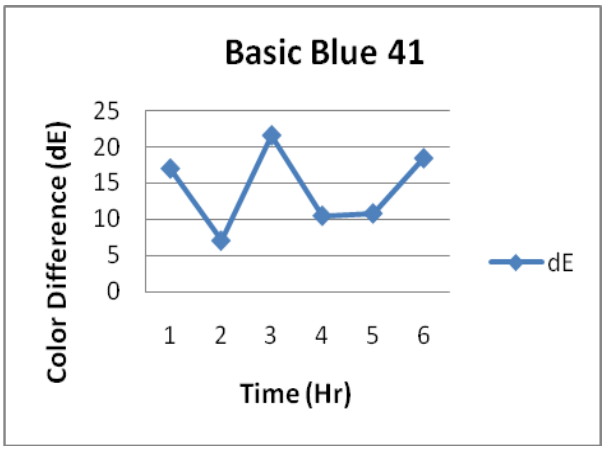


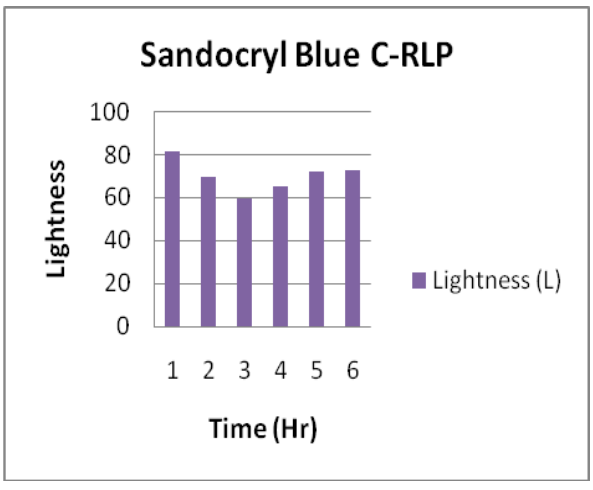


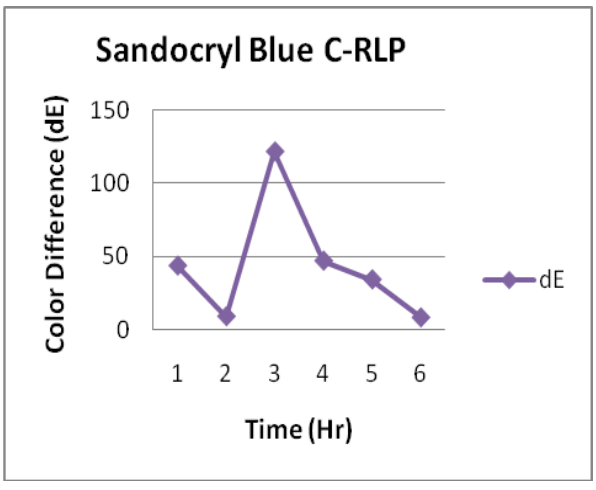
13. Basic blue 41





14. Basic blue





Discussion 2

The above graphs of Lightness vs Time clearly explains the differences of colour lightness at different fixation temperatures. The dyes which belong to the same class e.g disperse can not have the same lightness values due to dear differences in hue and chroma. Theoretically the lightness values should have increase or decreased constantly with the increase of fixation times, but in this case the values are flactuating the dependecy is not a straight line. This may be explained by the unstable behavior of the SOL GEL solvent in the open atmosphere. Further investigation must me done.

Same situation goes for the color differences dependecies. The colour difference values were calculated using the followingCIE76 formula:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

CONCLUSION

This is every simple method of colouration of glass fibers using the TMSPM solvent as a meduim of transporting dye molecules to the non-wettable surface of the fiber at the same time the dyes are able to be bonded to the fiber.

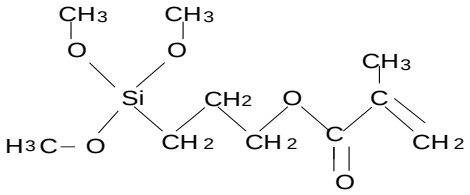


Figure 3.1: *chemical formula for TMSPM solvent*

This solvent is made by blending of 3-trimethoxysilyl propyl-methacrylate +isopropylanol with other complementary solvents; water, HCl and BPO, the bleding occurs at boiling point for about 30 minutes followed by cooling and further blending with Iso propylanol at 1:4 ratios. The solvent is only stable for few days and it has to be kept tightly sealed to prevent it from evaporating.

The TMSPM solvent forms a film on the fibre surface by means of bond creation through the Hydrogen from the CH_3 methyl groups which are bonded to the oxides of the solvent structure. Since the structure of glass fibre is composed of SiO_4, bonds are able to be formed and thus creating a film on the fibres surface which can be coloured by any Acids SO_3 Na (or −COONa), Disperse (−OH, $-NH_2$, $-SO_2NH_2$) and Cationic dyes ($-^{+}NH_2HCL^{-}$, $-^{+}NR_3\ Cl^{-}$) having suitable end groups which can react with the TMSPM and resulting to bond formations.

The information given above has not been scientifically been proven it is based on observations and fibre behaviour during treating with this TMSPM solvent. There were changes in the handle of the glass filter paper; it was stiffer which could be explained by the solvent forming a film on the surface of fibres. Overall the dye-fibre properties are moderate and bright shade and dark shades can be obtained using this solvent and a good selection of dyes, the glass fibres were not damaged.

RECORMANDATIONS

There should be more experiments and test performed in regards to this topic and about the type of solvent which is used. It is essential that more studies must be conducted to obtain much more concrete evidence about the solvent and suitable temperatures and time for dye fixation. The experiments conducted here were performed on Glass filter paper only, a use of different substrate may result to much more interesting results and facts. Overall its possible to use this solvent as the dyeing medium for high thermal fibres such as glass, aramides etc.

If one wants to use this solvent, one has to make sure that the container of this solvent is tightly sealed at all times in order to receive accurate results, after few days the solvent becomes weak, as a result the dyes become less soluble, which may results to visible staining by dye particles on the surface of the fabric and the overall dyeing will result to poor fastness properties and unlevel colours.

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APPENDIX

Table 4.4: The list of all 14 selected Dyes for fastness test properties

	Selected Dyes	**Code**	**C.I. name**	**C.I number**	**Solubility**
1	Maroon	RM	C.I Acid red	179	Soluble
2	Gold	GR	C.I Acid yellow	99	Soluble
3	Blue	GG	C.I Acid Blue	158	Soluble
4	Black	WAX	C.I Acid Black	52	Soluble
5	Brilliant Red	E-LB	C.I Disperse Red	60	Soluble
6	Gold	C-RLP	C.I Disperse yellow	42	Soluble
7	Gold	B-L5R	C.I Disperse yellow	23	Soluble
9	Blue	E-LG	C.I Disperse Blue	81	Soluble
10	Golden Yellow	C-GL	C.I Basic yellow	28	Soluble
11	Golden Yellow	GL-E	C.I Basic Yellow	28.	Soluble
13	Red	FBL	C.I Basic Red	46	Soluble
13	Red	GTLN	C.I Basic Red	18	Soluble
14	Blue	FGGL	C.I Basic Blue	41	Soluble
15	Blue	C-RLP	C.I Basic Blue	-	Soluble

Table 4.5: all dyestuffs which have been tested for wash fastness properties using the spectroscopy as the evaluating to*o*l

M. Complex	Acid red 179	Acid Yell 99	Acid Blue 158	Acid Black 52
Wavelength	504	450	624	570
absorbency	0.1	0.5	2.2	1.2

Disperse Dyes	Disperse Red 60	Disp Yellow 42	Disperse Yellow 23	Disperse Blue 81
Wavelength	400	406	400	582
absorbency	0,01	0.1	0.1	0.1

Cationic Dyes	Yellow 28	Yellow 28.	Red 46	Red 18	Blue 41	Blue -
Wavelength	402	396	524	486	486	600
absorbency	4	4	0.6	3.5	0.1	0.2

Table 4.6: light fastness results of first samples from the blue scale in ***Figure 4.11*** above at 20 minutes

Sample No	Results	Sample No	Results
1	1	9	2
2	2	10	3
3	3	11	3
4	3	12	3
5	3	13	4
6	3	14	1
7	4	15	2

Table 4.7: fastness results of second samples from the blue scale in ***Figure 4.12*** above at 120 minutes

Sample No	Results	Sample No	Results
1	1	9	1
2	3	10	3
3	2	11	2
4	2	12	2
5	2	13	3
6	2	14	1
7	3	15	1

Tables 4.8: results obtained from the spectroscopy for evaluation of the wash fastness using different fixation temperatures

M. Complex	Fixation	Red 179	Yellow 99	Blue 158	Black 52
Wavelength	Hours	504	450	624	570
absorbency	1	0. 141	0.650	1.627	0.646
	2	0.097	0.697	1.553	0.541
	3	0.213	0.460	1.727	0.690
	4	0.330	0.427	1.826	0.675
	5	0.135	0.605	1.634	0.518
	6	0.108	0.545	1.466	0.413

Disperse Dyes	Fixation	Red 60	Yellow 42	Yellow 23	Blue 81
Wavelength	Hours	400	406	400	582
absorbency	1	0.038	0.089	0.136	0.026
	2	0.036	0.138	0.110	0.028
	3	0.029	0.124	0.081	0.069
	4	0.032	0.098	0.076	0.024
	5	0.033	0.104	0.066	0.027
	6	0.58	0.094	0.099	0.022

Cationic Dyes	Fixation	Yellow 28	Yellow 28	Red 46	Red 18	Blue 41	Blue -
Wavelength	Hours	402	396	524	486	486	600
absorbency	1	3.555	3.503	0.744	1.904	0.046	0.008
	2	3.555	3.503	0.789	1.611	0.040	0.039
	3	3.497	3.503	0.725	1.530	0.036	0.091
	4	3.497	3.561	0.398	1.365	0.029	0.081
	5	3.497	3.561	0.496	1.564	0.050	0.038
	6	3.497	3.561	0.344	2.932	0.056	0.009

Table 4.9: Lightness values which are plot against time on the last graphs

M. Complex	Red 179	Yellow 99	Blue 158	Black 52
Time (Hr)	Lightness	L	L	L
1	84.16965	84.43567	51.74031	54.16005
2	84.81043	81.6009	54.29915	56.36668
3	85.99078	79.13242	53.05898	50.59958
4	86.26819	80.88869	47.92272	60.28436
5	86.06873	83.6076	55.54877	51.93432
6	86.69106	82.81451	53.60123	59.20076

Disperse Dyes	Red 60	Yellow 42	Yellow 23	Blue 81
Time (Hr)	Lightness	L	L	L
1	76.93675	89.04505	91.26789	72.20984
2	78.71204	72.45818	67.24361	85.74311
3	77.85838	89.76005	69.42403	80.57446
4	76.66587	89.31661	73.19169	83.64668
5	77.57002	89.08879	66.88711	71.9875
6	77.11618	89.03445	64.18977	83.93867

Cationic Dyes	Yellow 28	Yellow 28	Red 46	Red 18	Blue 41	Blue -
Time (Hr)	L	L	L	L	L	L
1	73.06397	62.86743	63.58809	52.70158	69.55777	81.43606
2	66.65479	73.8112	66.45123	54.07536	77.92583	72.35778
3	64.38348	72.19352	65.50256	53.61729	63.60372	59.88656
4	72.00643	73.92176	71.93883	55.07281	73.71247	65.31512
5	64.19294	73.37387	64.62976	54.25083	74.88648	69.89806
6	67.53121	73.43267	68.50877	53.54718	82.52834	72.85503

Table 4.10: colour difference values which are plot against time on the last graphs

M. Complex	Red 179	Yellow 99	Blue 158	Black 52
Time (Hr)	dE	dE	dE	dE
1	7.590214	41.03756	5.696207	4.193587
2	25.56576	47.13221	9.364917	2.268012
3	37.3458	10.3715	11.10772	1.915803
4	57.96757	7.073164	4.663597	10.37966
5	16.3647	17.88039	15.20826	6.7218
6	32.94984	23.72446	4.832673	9.683656

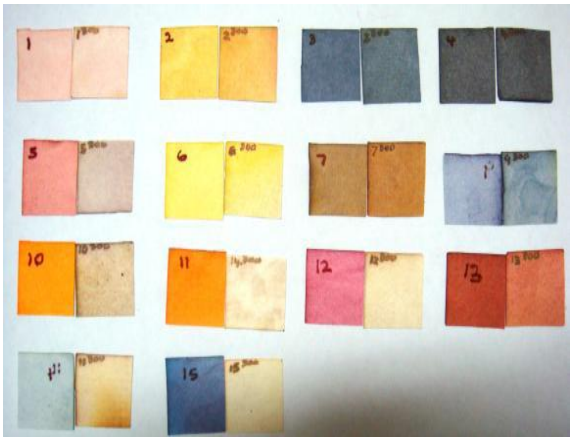
Disperse Dyes	Red 60	Yellow 42	Yellow 23	Blue 81
Time (Hr)	dE	dE	dE	dE
1	5.03472	272.0726	124.4238	72.48807
2	5.791951	26.60785	35.62793	5.79356
3	15.59095	11.32224	27.57728	44.7874
4	16.2344	14.79918	88.53432	46.01492
5	18.76909	24.92291	171.4604	67.80429
6	7.241636	31.22866	108.1873	53.81667

Cationic Dyes	Yellow 28	Yellow 28	Red 46	Red 18	Blue 41	Blue -
Time (Hr)	dE	dE	dE	dE	dE	dE
1	125.2356	24.07643	1099.191	28.78076	**16.94**	43.47883
2	68.44317	38.58571	868.587	29.58184	7.017	8.886937
3	56.47401	40.26516	876.3402	28.18419	21.51	121.2822
4	28.68513	89.32382	985.9704	31.43666	10.44	46.80171
5	33.6486	17.61418	699.8941	17.47803	10.77	34.02855
6	31.19315	27.77512	924.6533	23.03924	18.36314	8.093824

The following are the photos taken for high temperature fastnesses

200 C

300 C



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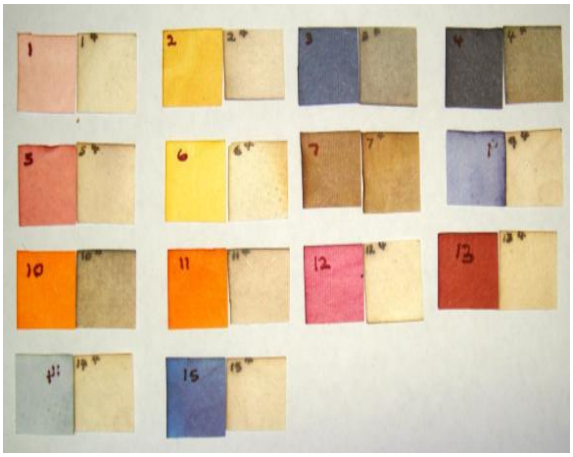

500C